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INVESTIGATION OF SURFACE COMBUSTION CONCEPTS FOR
NO_x CONTROL IN UTILITY BOILERS AND STATIONARY GAS
TURBINES

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AND STATIONARY GAS TURBINES**



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by

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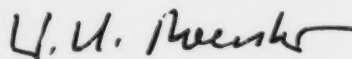
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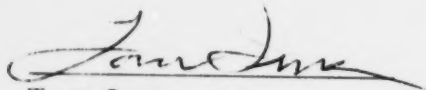
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ACRONYMS, TERMS, AND ABBREVIATIONS

AEC	Atomic Energy Commission
AFAPL	Air Force Aero Propulsion Laboratory
AGA	American Gas Association
AiResearch	AiResearch Manufacturing Company
American Lava	American Lava Corporation
APU	auxiliary power unit
CFR	Cooperative Fuel Research
Chrysler	Chrysler Corporation, Amplex Division
CO	carbon monoxide
Corning	Corning Glass Works
DuPont	E.I. DuPont de Nemours & Co., Inc.
EPA	Control Systems Laboratory, Environmental Protection Agency
EVC	externally vaporizing combustor
FID	flame ionization detector
Ford	Ford Motor Company
General Electric	General Electric Company, Space Division
General Motors	General Motors Corporation
HC	hydrocarbons
Holden	Holden Company
LEL	lower explosive limit
LPG	liquified petroleum gas
Matthey Bishop	Matthey Bishop, Inc.

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ACRONYMS, TERMS, AND ABBREVIATIONS (Cont)

NASA/Lewis	National Aeronautics and Space Administration, Lewis Research Center
NDIR	nondispersive infrared
NO _x	oxides of nitrogen (NO plus NO ₂)
Perfection	Perfection Products Company
Pratt & Whitney	Pratt & Whitney Aircraft Division, United Aircraft Corporation
Selas	Selas Corporation of America
TEL	tetraethyl lead compound (one of several lead compounds used in gasoline)

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SECTION 1

SUMMARY

Based on a review of the state of the art of surface combustion concepts, an assessment has been made of their applicability to large utility boilers and stationary gas turbines.

The term "surface combustion," as used in this study, refers to those concepts in which combustion occurs in close proximity to a solid surface. The interest in these concepts arises from their low-emission characteristics, in particular NO_x , which result from the combustion process occurring at reduced temperatures. This process can be either noncatalytic or catalytic. In the noncatalytic surface combustor, a fraction of the heat of combustion is immediately transferred from the flame layer to the adjacent solid surface. This heat is then removed from the burner surface by means of radiation and/or conduction into imbedded cooling tubes. This heat transfer mechanism results in gas temperatures below the adiabatic flame temperature. In the catalytic combustor, reduced gas temperatures are achieved by operation with very lean fuel-air mixtures. The catalyst serves the function of promoting chemical reactions, which, under these operating conditions, would otherwise occur too slowly for efficient low-emission burning.

1.1 STUDY RESULTS

The results of the investigation are summarized as follows:

1. Little information is available on the design and operational characteristics of catalytic combustors, except for some exploratory test work conducted by Engelhard Industries and by the Control Systems Laboratory of the Environmental Protection Agency. In these tests, extremely low NO_x emission levels have been achieved with concurrently low HC and CO emissions.

2. Emission test data obtained by Engelhard Industries on small-size catalytic combustors, operated with propane and gasoline, indicate undetectable NO_x , less than 60 ppm CO, and less than 10 ppm HC. These values are for fresh catalyst materials and do not include potential long-term performance degradation effects due to catalyst poisoning and high-temperature operation.
3. Further reduction of the HC and CO emissions might be achieved by increasing the operating temperature of the catalytic combustor and the residence time of the combustion products. Current state-of-the-art technology limits the temperature of catalysts to about 2400°F, but advanced monolithic or pellet substrates might be developed which have a higher temperature capability. At these temperature levels the NO_x emissions are still low.
4. The available information indicates that catalytic combustors might be applicable to both existing and new stationary gas turbines. However, a number of potential problem areas require resolution before a complete assessment of the feasibility of these devices can be made. Systematic and carefully planned experimental and theoretical investigations are recommended to provide the technical information needed for a meaningful evaluation of catalyst durability, specific heat release rate, emission characteristics, mechanical integrity, catalyst materials optimization, ignition characteristics, and pressure drop.
5. It is unlikely that catalytic combustors can be incorporated economically into existing utility boiler installations, which operate with little excess air. Since the catalyst requires a lean fuel-air mixture, several combustor stages would be needed with fuel addition and heat rejection between stages. A change in the boiler heat transfer mechanism from primarily radiative to primarily convective would be involved which, in turn, would require a complete redesign of the boiler and its air induction system. The concept might be feasible for newly designed power plants, but additional preliminary design studies would have to be carried out to resolve this issue.
6. No information is presently available regarding the application of noncatalytic surface combustors, of the flow-through or direct-fired types, to large utility boilers. However, theory and limited small-scale burner experiments indicate that a surface combustor has the potential of achieving NO_x emission levels appreciably lower than those obtained in the best current state-of-the-art large utility boilers. Due to the large surface area requirements of these combustors, novel design configurations must be utilized to accommodate the burner within the boiler envelope. Although

the porous-plate surface combustor concept might be technically feasible, it lacks attractiveness because of limited fuel compatibility and complex problems of packaging. The porous-plate combustor may not be the optimum concept for removing heat from the flame zone.

7. Porous-plate surface combustors require large burner surface areas and volumes. For example, for an equivalence ratio of unity, a system pressure of 1 atmosphere, and a gas temperature of 3000°F, the cooling capacity of porous-plate burners is about 45,000 Btu/hr-ft², resulting in a surface area requirement of about 20,000 ft² for a typical utility plant (300 MW output).
8. NO_x emissions below 40 ppm are predicted for noncatalytic surface combustors operated at typical steam boiler conditions and maximum gas temperatures of 3000°F. Preliminary test data by General Electric are in reasonable agreement with the NO_x prediction. The CO emissions from those tests are of the order of 500 ppm.
9. Sintered porous metal surface combustors incorporating imbedded cooling tubes represent a design approach which merits further evaluation for low-pressure gas turbines of the type projected for automotive and highly regenerated stationary gas turbines, and possibly combined gas turbine/steam turbine cycles. However, because of the high heat loads and surface temperatures resulting from the high system pressures of typical simple-cycle gas turbines, porous-plate surface combustors are not considered feasible for this particular engine type.
10. Porous ceramic surface combustors are not considered feasible for use in either simple-cycle or regenerative-cycle gas turbines, because acceptable burner surface and gas temperatures require the application of imbedded cooling tubes. However, because of the large differences in thermal coefficients of expansion of ceramics and metals and the consequent excessive thermal stress, incorporation of cooling tubes is not currently possible.
11. Before a complete assessment of porous-plate surface combustors can be made, substantial research and development efforts are required to demonstrate satisfactory burner operation for long periods of time in an environment typical of large utility boilers and gas turbines, without clogging of the micron-size pores.
12. To prevent fuel coking and local overheating of the burner materials, catalytic and porous-plate surface combustors are limited to premixed gaseous and prevaporized, premixed distillate fuels. The sulfur and metal content of the fuel must be maintained at

very low, but as yet undetermined, levels to minimize poisoning of the active catalyst and clogging of the micron-size porous burner pores.

13. In premixed/prevaporized systems, preignition of the combustible mixture presents a potential problem area, if the mixture temperature is higher than the autoignition temperature of the fuel. With methane, preignition could occur in highly regenerated gas turbines (with pressure ratios of the order of 4 to 6) and high pressure ratio simple-cycle gas turbines, unless special care is exercised in the design of the fuel prevaporization and mixing chamber. For kerosene-air mixtures, the autoignition temperatures and the ignition delay times are low enough that preignition could occur in all gas turbines. In steam boilers, the autoignition temperatures of methane and kerosene are above the typical air preheat temperatures of about 650°F. Therefore, preignition does not pose a problem in well designed induction systems.
14. Either monolithic or pellet type substrates are considered applicable to catalytic combustors. The catalyst and substrate composition and manufacturing processes are considered proprietary by the manufacturers. Currently, platinum group metals are favored for automotive oxidation catalysts, but base metal or promoted base metal formulations might be developed for use in second-generation catalysts. The noble metal content of the promoted catalyst formulation is expected to be sufficiently low so as to have no significant impact on the world platinum group metal supply and demand balance.

1.2 CONCLUSIONS

In summary, it is concluded that the catalytic combustor concept looks promising for application in gas turbines. However, comprehensive experimental and theoretical investigations are required to provide the information needed for a meaningful assessment of this concept. Catalytic combustors are not considered feasible for use in existing steam boilers, but might be applicable to newly designed installations.

The sintered metal porous-plate combustor concept with imbedded cooling tubes, while technically feasible for steam boilers and possibly for low pressure ratio gas turbines, lacks attractiveness because of packaging problems and the requirement of gaseous and distillate fuels.

SECTION 2

INTRODUCTION

The purpose of this report is to present a review of the state of the art of surface combustion concepts and an assessment of their applicability to large utility boilers and stationary gas turbines.

The term "surface combustion," as used in this study, refers to those concepts in which combustion occurs in close proximity to a solid surface. The interest in these concepts arises from their low emission characteristics, in particular NO_x , which result from the combustion process occurring at reduced temperatures. This process can be either noncatalytic or catalytic. In the noncatalytic surface combustor, a fraction of the heat of combustion is immediately transferred from the flame layer to the adjacent solid surface. This heat is then removed from the burner surface by means of radiation and/or conduction into imbedded cooling tubes. This heat transfer mechanism results in gas temperatures below the adiabatic flame temperature. In the catalytic combustor, reduced gas temperatures are achieved by operation with very lean fuel-air mixtures. The catalyst serves the function of promoting chemical reactions, which, under these operating conditions, would otherwise occur too slowly for efficient low-emission burning.

Surface combustion devices have been in wide use for industrial heating and chemical process applications, and low-temperature catalytic combustors have long been used for space heaters. Because of their potential for achieving very low NO_x emissions, these devices have recently received considerable attention with respect to application in gas turbines as well as Rankine cycle engines. This study will review these recent activities to determine whether a potential exists for applications in utility boilers and stationary gas turbines, and, if so, to identify potential problem areas and to delineate further research efforts necessary for their resolution.

The technical data presented in this report are based on discussions with a number of organizations that are active in the area of surface combustion research, development, and manufacture. The information is supplemented by material from contractor reports and other literature related to the general subject.

The results of this study are presented in the following manner: Sections 3 and 4 include state-of-the-art reviews of noncatalytic and catalytic surface combustion devices, respectively; Section 5 treats the evaluation of these devices for large utility boilers; and Section 6 is concerned with an evaluation of these concepts as applied to stationary gas turbines. Appendix A lists the organizations that were contacted during the course of this investigation. Appendix B presents a table of metric conversion factors.

SECTION 3

STATE-OF-THE-ART REVIEW OF NONCATALYTIC SURFACE COMBUSTION DEVICES

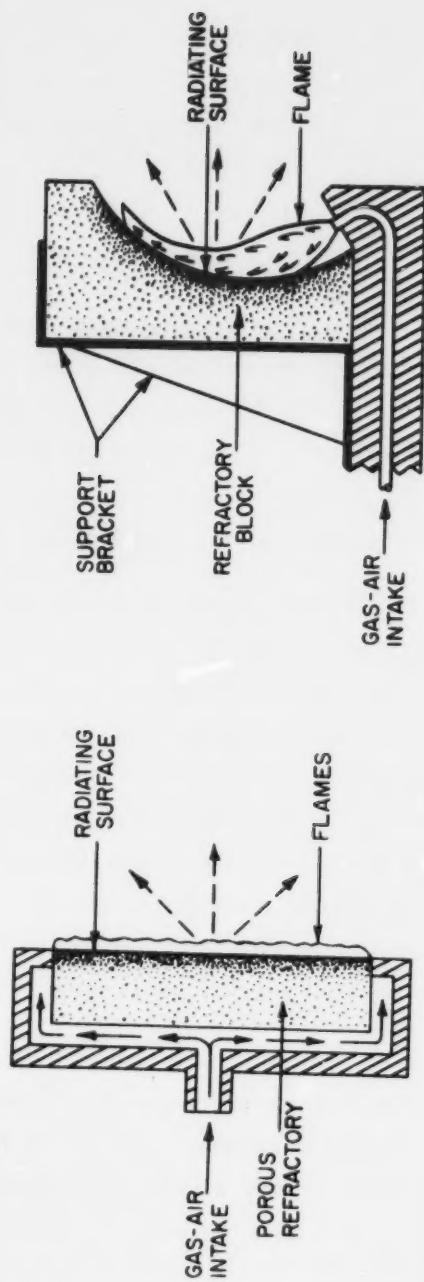
3.1 INTRODUCTION

The technical information presented in this section is based on material extracted from the literature and from the discussions with a number of organizations known to be involved in the development and manufacture of noncatalytic surface combustion devices. These include primarily the American Gas Association, U. S. Bureau of Mines, Burnham Corporation, General Electric Company, Selas Corporation, and University of Wisconsin.

In the broadest sense, the term "surface combustion" involves the promotion of gas-phase oxidation and reduction reactions between fuel and air in close proximity with a solid surface. Surface combustors, which are also known by several other designations such as nonadiabatic, flat-flame, radiant, refractory, and infrared burners, have shown promise as low-pollution devices. In these burners, a fraction of the heat of combustion is immediately transferred from the flame layer to the solid surface, which generally consists of a porous metallic or refractory ceramic material. The energy transfer is adjusted such that the combustion temperature is reduced sufficiently to limit the formation of NO_x emissions without significantly compromising the CO and HC oxidation reactions.

Basically, there are two surface combustor concepts, classified as (1) flow-through or transpiration burners, and (2) direct-contact radiant burners. The design features of these two configurations, shown in Figure 3-1, are briefly discussed as follows:

The flow-through burner consists of a porous plate which is comprised of either an open-celled matrix of closely spaced interstices or ports which



Flow-Through (Transpiration) Porous Burner

Direct-Contact Radiant Burner

Figure 3-1. Surface Burner Configurations

allow the passage of the fuel-air mixture. These burners, which require a prevaporized and premixed fuel-air charge, are limited to gaseous and distillate liquid fuels. The pore structure depends upon the fabrication methods which include laminating, foaming, blowing, and powder or granule bonding. Metallic or refractory ceramic materials are used in the manufacture of the burner plates, which can be made in the form of flat plates, cylinders, and hemispheres.

In the direct-contact burners, the fuel-air mixture is discharged through a set of nozzles in such a manner that combustion occurs along a refractory surface. Gaseous fuel-air mixtures are preferred for these burners, but they can be modified to handle certain liquid fuels.

Porous refractory surface combustors are used commercially in various applications including dryers, space heaters, and metal treating and brazing systems. Also, experimental combustors of the metallic and ceramic types are currently being developed for potential use in automotive gas turbine and Rankine cycle engines.

Exploratory work on surface combustion was conducted as early as 1820, with experiments to induce chemical reactions in air-gas mixtures below their ignition points on the surface of solid materials. In 1902, W. A. Bone began systematic investigations on the effect of hot surfaces on combustion (Ref. 3-1). By 1907, his experiments had shown that (1) hot surfaces have the capability of accelerating combustion of gaseous fuel-air mixtures, (2) the chemical reactions are confined to the boundary layer region between the gaseous and solid phases, (3) the accelerating effect of a hot surface on combustion increases with increasing temperature, and (4) surface combustion depends upon adsorption of the combustible mixture on the surface whereby it becomes "activated" by association with the surface. Based on these considerations, Bone concluded that if a gaseous fuel-air mixture is passed through a porous refractory material under suitable conditions, combustion would take place very rapidly in a thin layer adjacent to the surface of the plate. The heat released during combustion maintains the surface in a

state of incandescence without a visible flame, thus realizing the idea of a flameless, incandescent surface combustion. According to Bone, the principal advantages of this concept include the capability of efficient combustion with a minimum of excess air and uniform heat transmission from the incandescent surface by means of radiation.

The surface combustion concept has since been further developed by Bone and by others and is currently applied in various industrial heater designs. More recently, the concept has generated considerable interest because of its low NO_x emission potential.

The theory supporting the contention that surface combustion can diminish pollution emissions stems from the present knowledge of post-flame combustion gas behavior, taking into account the combustion energy release and heat transfer mechanisms. The detailed steps in the chemical transformations are not fully understood, but are founded in classical thermodynamic and kinetic theories. Many of the arguments focus attention on the formation and accumulation of nitrogen oxides, particularly NO, in burner gases. The earliest theories presumed the establishment of equilibrium between molecular nitrogen and oxygen within the post-flame, high-temperature region of a combustor. Difficulty quickly became apparent with this simplified approach because practical combustors rarely provide sufficient residence time for equilibrium concentrations to be attained. Efforts were then directed to nitric oxide kinetic models. NO concentrations computed by means of the Zeldovich model, which describes the rates of thermal fixation acquired through atomic oxygen-nitrogen interactions in the post-flame gases, are presented in Figure 3-2 as a function of stoichiometry, selected combustion temperature, and residence time (Ref. 3-2).

The simple Zeldovich mechanism is adequate to predict the NO formation rates at high temperatures. However, at temperatures below approximately 1500°K , the actual NO formation rates are substantially higher than those predicted by the Zeldovich model (Refs. 3-3 and 3-4). Under these

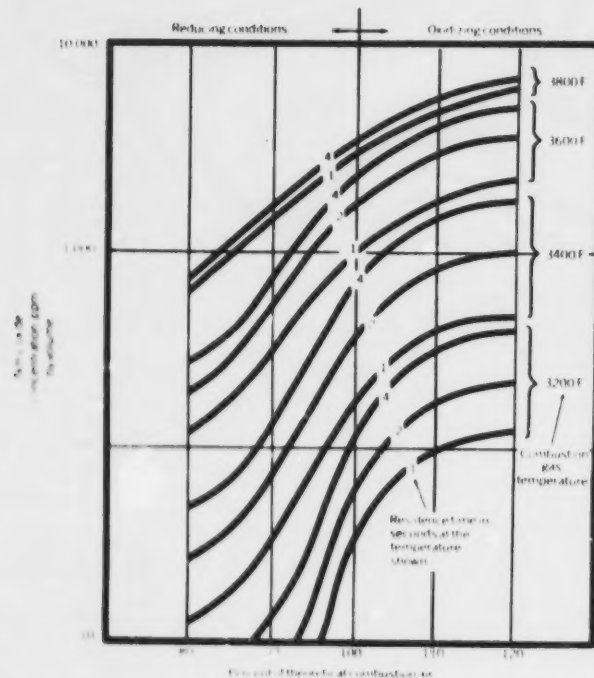


Figure 3-2. Kinetic Data--Natural Gas Fuel (Ref. 3-2)

conditions, the mechanism involving N_2O can no longer be neglected. As indicated in Figure 3-2, the formation of NO_x , which is exponentially related to the combustion temperature, can be reduced substantially by lowering the flame temperature. In surface combustion, this can be accomplished by dissipating a fraction of the total heat of combustion by means of radiation from the incandescent surface or conduction into imbedded cooling tubes. In either of these approaches, the adiabatic combustion temperature is not attained and, for this reason, these burners are also known as nonadiabatic burners.

3.2

STATE-OF-THE-ART REVIEW

Following is a review of the state of the art, presented by organization:

3.2.1 American Gas Association

The combustion-related R&D work currently being conducted by the American Gas Association (AGA) laboratories is directed toward the development and evaluation of refractory porous-plate-type radiant burners for potential use in household applications (Ref. 3-5).

3.2.1.1 Combustor Design Features

The refractory burners tested by AGA to date are of the porous-plate type, the drilled-port plate type, and the direct-fired type. In the porous-plate and drilled-port configurations, the air-gas mixture flows through the plate at low velocities. Conversely, the direct-fired burner utilizes a blower to supply the fuel-air mixture, which is burned so that the flame impinges on the refractory burner face (Ref. 3-6). The burners have a temperature capability of about 2000°F. Although AGA is not interested in higher temperatures for its applications, at least one of these burners has been tested up to 2300°F. AGA feels that the maximum temperature of the burner is limited only by the capability of the refractory material. However, cracking of burner plates may pose serious problems at these higher temperatures.

3.2.1.2 Operational Characteristics

The refractory burner test work at AGA is limited to gaseous fuels, including natural gas, liquefied petroleum gas, and manufactured natural gas. The manufactured gas is obtained by cracking natural gas and consists of CO and H₂ and some CH₄ which is added after the cracking process to adjust the heating value to 530 Btu/std ft³. According to AGA, this heating value is required to satisfy the appliance code, which was written many years ago when the gas supplied by the producers was of that type.

The burner tests conducted by AGA are based on fuel-air equivalence ratios between 0.9 and 1.1. For efficiency reasons, they are not interested in fuel-air ratios outside this range. The pressure drop of the burners is dependent upon the porosity of the refractory plate material and the flow rate used in the particular application, and is of the order of 4 to 5 inches of water. With respect to turndown ratio of these burners, AGA states that a factor of 3:1 can be easily realized by means of inlet flow throttling. Further turndown could be achieved by shutting off individual sections of the burner (sectional burner design). The burner is lighted by means of a pilot light or electric spark or glow plug. Since the AGA programs are limited to gaseous fuels, there are no problems related to fuel vaporization and air-gas mixture non-uniformity. After lightoff, the burner operates with a blue flame, approximately 3/8 inch high.

Apparently, under normal operating conditions ($<1850^{\circ}\text{F}$), thermal shocks have never been a problem with the type of refractory materials used in the AGA test programs. Cyclic durability tests (15-minute on/off cycles) extending over several years have been conducted on some of these burners without incurring a failure. However, some cracking of the refractory material has been observed within several hours of cyclic operation at temperatures above 2100°F .

3.2.1.3 Heat Transfer Characteristics

Radiation test data from a number of gas-fired infrared burners show heat release rates between 14,000 and 63,000 Btu/hr-ft², depending upon the burner design, surface temperature, and combined emissivity of the burner surface and the "flame" layer adjacent to that surface.

In 1966, development work on a compact radiant burner projected for use in a refrigerant boiler was initiated by the AGA (Ref. 3-7). This burner-boiler design consisted of two rectangular refractory burners and a "coolant wall" located between the two burner surfaces. Each burner had a surface area of

0.85 ft². The unit was operated on natural gas with about 8 percent excess air, at a surface temperature of 1800°F and an estimated flue gas temperature of about 2200°F. Based on an emissivity of 0.8, the design radiant heat flux of this unit was 36,000 Btu/hr-ft². The total heat flux of the unit was 54,000 Btu/hr-ft², indicating that about 1/3 of the total heat of combustion was transferred to the coolant wall by means of radiation.

3.2.1.4 Emission Characteristics

Average NO_x and CO emission test data for refractory and conventional burners tested by the AGA are listed in Table 3-1. (Ref. 3-5)

The data in the table indicate that the NO_x emitted from the AGA infrared burner is only about 10 percent of that obtained with conventional burners and about 1/3 of that of commercially available infrared burners. Conversely, the CO emissions of the commercial infrared burners are approximately three times higher than from conventional burners. However, AGA feels that the higher CO emission levels of the radiant burners would probably be acceptable from an air quality and health effects point of view.

3.2.2 Bureau of Mines

The Bureau of Mines has conducted an investigation of the emission characteristics of three different burner concepts designed to simulate the operation

Table 3-1. NO_x and CO Emissions of Conventional and Infrared Burners

Burner Type	Emissions, ppm (corrected to stoichiometric)			
	NO	NO ₂	NO _x	CO
Conventional	78	16	94	91
AGA infrared	9	0	9	N. A.
Commercially available infrared	12	12	24	293

of gas appliances such as space heaters and water heaters (Ref. 3-8). These burners, including a flat-flame Meeker burner, a ceramic infrared plate burner, and a multiport ring burner, were operated at lean, stoichiometric, and rich fuel-air ratios using methane as test fuel. The Meeker burner was also operated on propane and a mixture of propane and recycle gas to simulate the effects of flue gas recirculation on the emissions.

3.2.2.1 Burner Design Features and Operation

The Meeker burner test setup is presented in Figure 3-3. As indicated, the burner consists of a 3/8-inch-high stainless steel grid with 1/8-inch-square openings. The port is surrounded by a water-cooled steel tube arrangement. The flame and burner tubes were enclosed in a cylindrical steel duct equipped with a viewing window on one side and a traversing slit for probes on the other side. The primary flow rate through the burner was about $4.5 \text{ ft}^3/\text{min}$, resulting in a mixture velocity of 20 in/sec at the burner port. Secondary air was supplied through a calming bed at a rate of $3.7 \text{ ft}^3/\text{min}$, corresponding to an axial velocity of 5 in/sec. In operation, the small conical flames emerging from the square openings of the burner approximate a flat flame, about 0.10 inch high.

The ceramic infrared burner used in the program consists of a 5×7 inch plate composed of 0.05-inch holes uniformly arranged at a rate of 210 holes/ in^2 . The burner was installed in a 9.5×12 -inch duct. The premixed flow rate through the burner was $4.5 \text{ ft}^3/\text{min}$, corresponding to a velocity of 3.7 in/sec at the port. Secondary air was admitted coaxially through a calming bed at a rate of $3.9 \text{ ft}^3/\text{min}$ and a velocity of 1.4 in/sec.

Both burners were operated at primary flow fuel-air equivalence ratios of 0.85, 1.0, and 1.2. The gas samples extracted from the burner at various axial and radial positions were analyzed for NO_x , CO, HC, and CO_2 . The NO concentrations were measured by the phenoldisulfuric acid method, HC was determined in a flame ionization detector gas chromatograph, and CO_2 by means of an activated charcoal column.

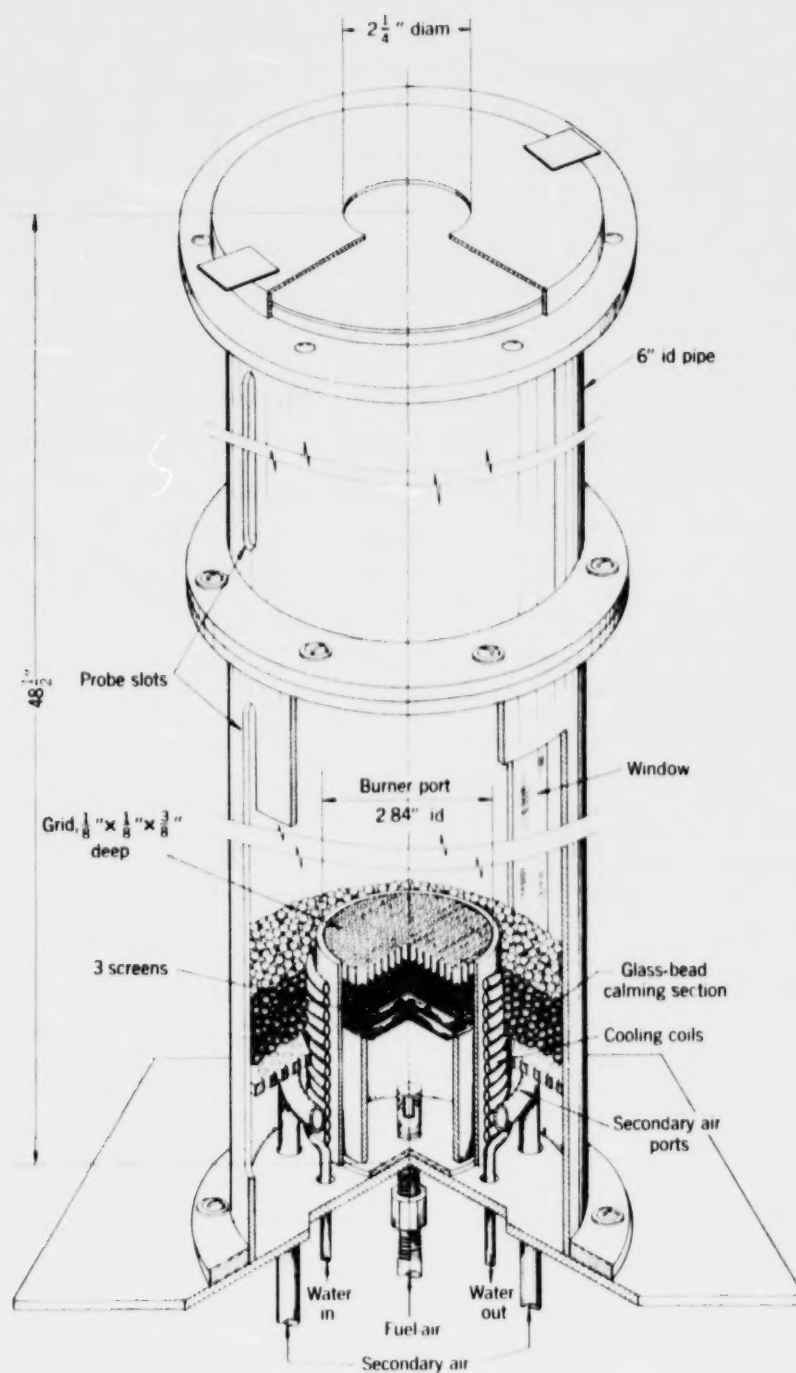


Figure 3-3. Bureau of Mines Flat-Flame Meeker Burner Test Setup (Ref. 2-8)

3.2.2.2 Emission Characteristics

The peak concentrations of NO and CO of the two-burner types are presented in Table 3-2. As indicated, the emissions of the infrared ceramic burner are always lower than the emissions from the Meeker burner. In the infrared burner, the measured NO_x concentrations are essentially equal at the burner surface and at a distance of 1 inch above the surface, reflecting the lower temperature level of the infrared burner. Conversely, the NO_x concentration of the Meeker burner increases substantially with increasing distance from the burner surface. This is due to the fact that the NO concentration is roughly proportional to the residence time. In both burners, the gas temperatures are sufficiently high to achieve substantial reduction of CO and HC within 1 inch of the burner surface. For fuel-rich mixtures, the CO remains very high because of a lack of sufficient oxygen at this condition.

3.2.3 Burnham Corporation

The Burnham Corporation manufactures commercial water boilers for home and industrial usage, and markets a line of patented dual-fuel (liquid-gas)-powered burners for various applications (Ref. 3-9). According to Burnham, these burners achieve low pollution combustion and better fuel economy than comparable conventional burners.

3.2.3.1 Combustor Design Features

Figure 3-4 is a sectional view of the Burnham dual-fuel burner concept. The burner is comprised of an air inlet nozzle, a startup manifold, a main fuel inlet manifold, and an igniter spark plug mounted to an attachment plate. The discharge side of the burner is a cube-shaped cast silica-alumina refractory tile containing the diverging combustion section and a hot gas recirculation tube.

Table 3-2. Peak NO_x, CO, and HC Concentrations and Flame Temperatures for Meeker Noninfrared and Ceramic Infrared Burners--Methane-Air Mixtures

Vertical Distance from Burner Surface, inches	Temperature, °F		NO _x Concentration, ppm		CO Concentration, ppm		Total Hydrocarbons, ppm	
	Non-infrared	Infrared	Non-infrared	Infrared	Non-infrared	Infrared	Non-infrared	Infrared
LEAN FLAMES ^a (equivalence ratio 0.85)								
0	2,950 ^b	2,650	10	10	3,300 ^b	2,600 ^b	72,900 ^b	750 ^b
1.0	2,940	2,410	30	10	400	0	0	0
STOICHIOMETRIC FLAMES ^a								
0	3,380 ^b	2,930	40	10	23,500 ^b	6,700	22,660 ^b	370 ^c
1.0	3,210	2,580	100	20	3,100	700	0	0
-	-	-	230 ^b	-	-	-	-	-
RICH FLAMES ^c (equivalence ratio 1.20)								
0	3,320 ^b	2,790	50	30	41,100 ^b	36,500	42,415 ^b	310
1.0	3,150	2,720	80 ^b	30	39,100	34,000	0	0

^aConcentrations corrected for dilution with secondary air

^bPeak temperatures and peak concentrations of pollutants for burner

^cConcentrations not corrected for dilution with secondary air

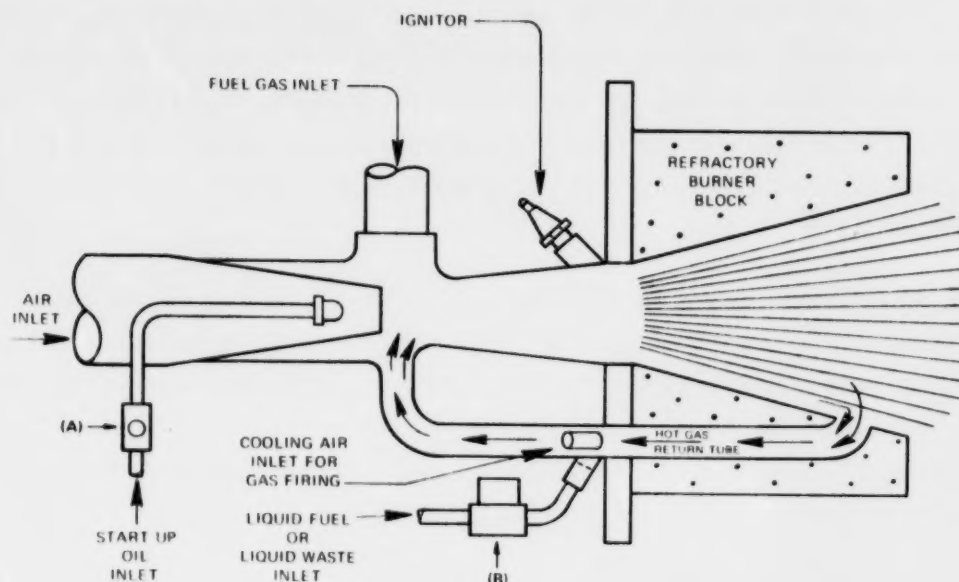


Figure 3-4. Burnham Dual Fuel Burner Sectional Schematic

3.2.3.2 Operational Characteristics

According to Burnham, several inherent advantages accrue to this type of burner configuration, which can operate on either gaseous or liquid fuels independently or simultaneously. Burnham states that combustion takes place mainly along the hot refractory walls. The burner operates on an induction principle designed to obtain good mixing of the fuel and air ahead of the flame zone. Pre vaporization of liquid fuel is accomplished through heat exchange with (about 10 percent) recycled products of combustion which are drawn through the return tube by differential pressure forces. This eliminates the need for a sophisticated spray atomization system. The principal features of the recycle gas vaporization, turbulent mixing, incandescent refractory wall combustion concept are (1) efficient and uniform transparent flame combustion for both gaseous and liquid fuels, and (2) low HC, CO, NO, and particulate emissions.

Fuels generally used in these burners include natural gas and other gases, jet fuel, kerosene, and No. 2 fuel oil. Fuels such as Nos. 4 and 5 oils are more difficult to vaporize, but have been successfully burned in these combustors. Some exploratory tests with powdered coal have been conducted to show feasibility of clean combustion to white ash. Burner turndown ratios are nominally 3:1.

During initial development and early production, cracking of the cast refractory materials was encountered. The curing methods have since been revised and this problem has been eliminated. With liquid fuels, carbon deposition has occurred in the return tube. However, the carbon can be burned out simply by switching to gaseous fuels for some time. There have been no maintenance problems with these burners other than infrequent spark plug replacement.

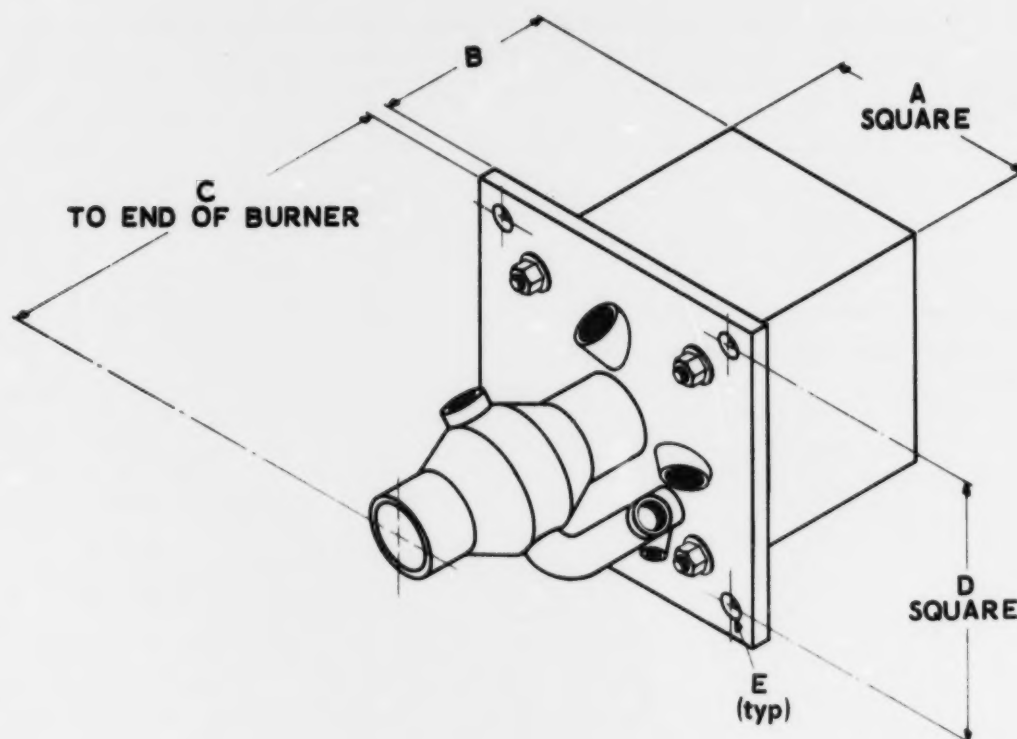
3.2.3.3 Heat Transfer Characteristics

The presence of an incandescent refractory surface allows a portion of the total heat of combustion to be transferred by radiation. Estimates by Burnham vary between 10 and 15 percent of the total heat release of the burner.

As shown in Figure 3-5, various sizes and operating ranges of Burnham industrial burners are available, ranging from 0.3×10^6 Btu/hr to 15×10^6 Btu/hr. Based on the overall dimensions of the refractory burner cube, the specific heat release rates are of the order of 3 to 5×10^6 Btu/hr-ft³.

3.2.3.4 Emission Characteristics

Tests have been performed on a Burnham boiler rated at 80 hp, using a model B030 burner and No. 2 fuel oil. These tests, which were conducted in 1971 by the Scott Research Laboratories, verified previous effluent results obtained on individual burners by another laboratory. In the Scott tests, flue gas samples were collected and were later subjected to analysis. A summary of the results is contained in Table 3-3.



DIMENSIONS and RATINGS

BURNER MODEL	MAX FIRING CAPACITY		A	B	C	D	E
	OIL GPH	GAS MBH					
B002	2.25	315	5"	5 1/2"	9 1/2"	6"	1/2" D
B005	6.5	910	7"	9"	15"	8 1/2"	1/2" D
B010	17	2,380	9"	9"	19"	10"	9/16" D
B030	50	7,000	12 3/4"	12 1/8"	16"	11 1/4"	5/8" D
B090	110	15,400	22 1/2"	16 1/2"	27"	*	3/4" D

* See certified drawings for details and exact dimensions of air and oil inlets, and mounting details.

Figure 3-5. Burnham Corporation Burner Dimensions and Ratings

Table 3-3. Operating Conditions and NO_x Emissions for a Commercial Boiler with Radiant Burner (Model PB-340 Boiler; Burnham B030 Burner)

Fuel Type	No. 2 Fuel Oil
Heating Value	19,530 Btu/lb
Flow Rate	25.7 gal/hr
Heat Flux	2.75×10^6 Btu/hr-ft ³
Flue Gas Composition (Avg.)	
CO ₂ , %	13.5
O ₂ , %	3
SO _x , ppm	81
NO _x , ppm	126
CH ₄ , ppm	5
Calculated NO ₂ Emission,	
lb/10 ⁶ Btu	0.2

The NO_x emissions listed for the Burnham burner are substantially lower than the NO_x levels of about 300 to 700 ppm emitted from conventional uncontrolled utility boilers. However, when comparing the NO_x emissions of the various burner-boiler designs, consideration must be given to the fact that the Burnham burner utilizes about 10 percent flue gas recirculation. Tests conducted by Southern California Edison Company (Ref. 3-10) and Combustion Engineering Company (Ref. 3-11) on gas-fired utility boilers indicate that flue gas recirculation is an effective means of reducing the NO_x emissions from conventional boiler units. This is illustrated in Figure 3-6, showing measured NO concentrations as a function of gas recirculation rate for corner-fired installations (Ref. 3-10). At 10 percent recirculation, the NO_x emissions of these utility boilers are of the order of 150 ppm. This indicates that the relatively low NO_x level achieved in the Burnham combustor might be primarily the result of flue gas recirculation, and not due to the refractory burner block design.

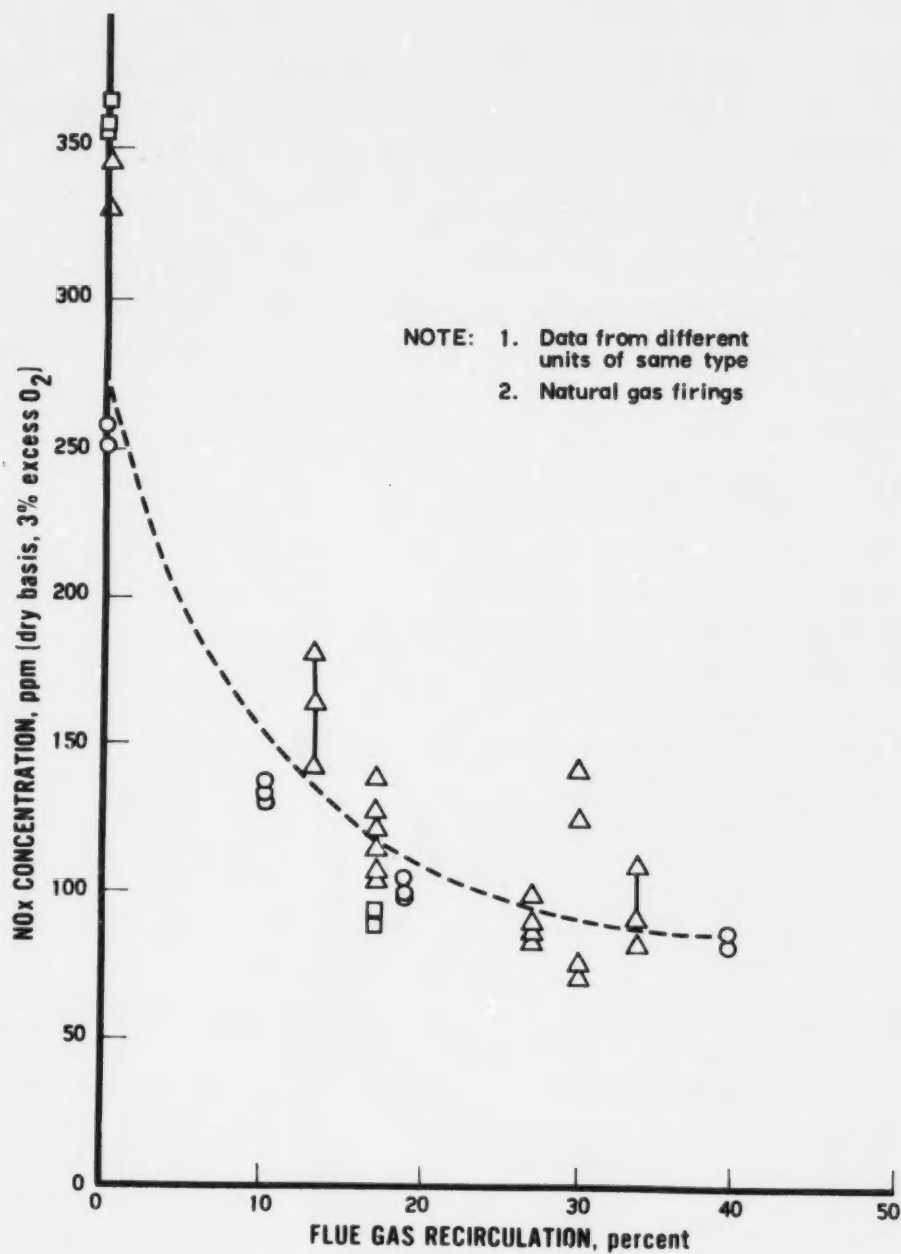


Figure 3-6. NO_x Emission Concentration vs Percent Flue Gas Recirculation--320 MW Corner Fired Unit (Ref. 3-10)

3.2.3.5 Burner Costs

The Burnham burner models are the only commercial devices where cost data were made available. The breakdown summary of unit costs for several burner models purchased in quantities is given in Table 3-4.

3.2.4 General Electric Company

The Space Division of General Electric is currently involved in the development of low-emission porous burners under both in-house and EPA-funded projects. The funded work is aimed at automotive gas turbine and Rankine cycle engines, and the in-house work involves porous flow-through burners for potential use in steam power plant boilers (Refs. 3-12 and 3-13).

3.2.4.1 Combustor Design Features

Conceptually, the General Electric burner consists of a porous, open-celled matrix usually configured as a right circular cylinder in system application design studies. Flat porous plates also have been used as test components. As illustrated in Figure 3-7, a mixture of air and fuel, premixed to the

Table 3-4. Burnham Burner Cost Data

Model Number	Burner Rating (Btu/hr) $\times 10^{-6}$	Basic ^a Burner Price \$	Auxiliary ^b Components Price \$	Total Assembled Cost \$
B002	0.3	200	530	730
B005	0.9	260	680	940
B010	2.4	310	710	1020
B030	7.0	730	900	1630
B090	15.5	1210	1250	2460

^aQuantity purchase price/unit

^bValves, fittings, igniter, electrical controls, etc., fitted for multifuel operation

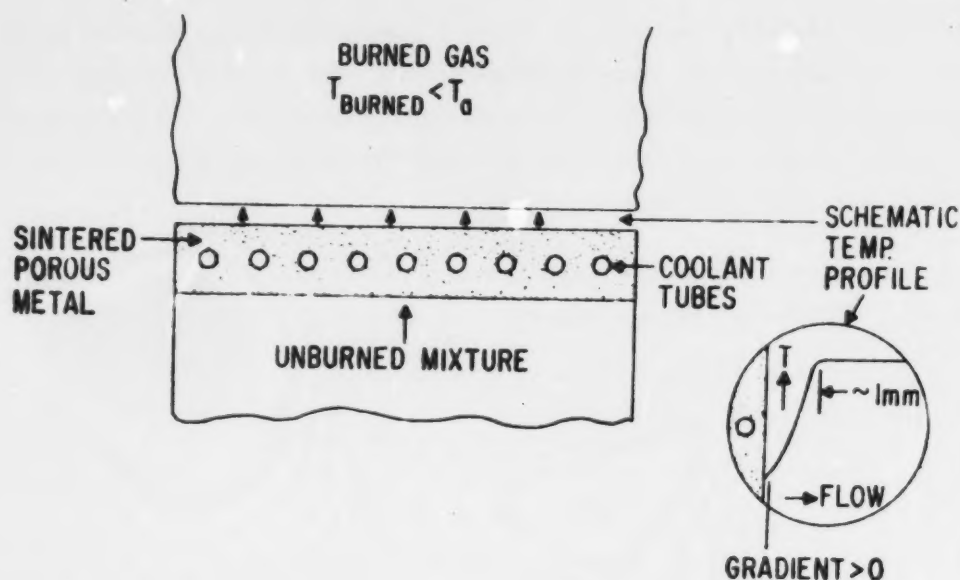


Figure 3-7. Schematic of Porous-Plate Burner (Ref. 3-13)

desired proportions (usually lean), is introduced to the burner through an inlet manifold. As the gases pass through the interstices of the porous matrix, they are preheated to ignition by absorption of thermal energy which has been liberated at the flame front. The flame front is considered to be positioned immediately beyond the exit (downstream) surface of the burner.

For automotive gas turbines, experiments have been made by General Electric with porous matrixes formed from various materials. So far, it has not been possible to find a single material capable of meeting all the operating requirements. These requirements include long life at high operating temperatures (2200°F to 2300°F), low thermal conductivity, good resistance to thermal shock and thermal stress, and oxidation resistance. Powdered metal alloys or refractory particle compositions are used. These can be formed to the desired shapes, commonly by compression molding. The structural integrity of the finished part is achieved by sintering with or without use of bonding

materials. Metallic burners have been fabricated from various steel, chromium, and nickel powder compositions. Ceramic materials considered by General Electric include silicon carbide and alumina-silica compositions. Composite laminates, comprised of a mullite base and a thin silicon carbide overlay, are commercially available.

Four possible porous burner configurations for gas turbines are shown in Figure 3-8 (Ref. 3-13), as follows:

1. A simple cylinder.
2. A composite structure consisting of a high-temperature, high-conductivity (silicon carbide) outer material and a low-conductivity inner material that is shown to be circumferentially segmented with the segments joined at wedging surfaces loaded by expansion springs.
3. A segmented structure, the pieces of which are made from an integrally bonded combination of a high-temperature, high-conductivity outer material and a low-conductivity inner material. The radial joints are pressurized at the ends by conically cut rings to which axial compression is applied by a spring.
4. An alternate segmented structure made from composite material pieces, as in the third configuration. The segment joints are pressurized by containment, at the ends, of alternate segments between outer cylinders and inner expansion springs. Experience has indicated that a small leakage flow between the pressurized joints is, under normal (sub-liftoff) operation, indistinguishable from the normal flow through the porous burner.

Figure 3-9 shows a conceptual combustor design for potential use in a gas turbine. Principal parts of the combustor include the outer containment shell; the radiation heat sink screen and support baffle; the segmented porous burner structure; the forward end burner support structure with its axial loading spring; the aft end burner support structure, with the integrally attached primary fuel-air mixing tube; the fore and aft radial expansion springs for pressurizing the burner segment joints; the vaporizer, which incorporates the air atomizing nozzle; and the primary air-flow control valve with actuator. Heated atomizing-vaporizing air and fuel are introduced into the air atomizing

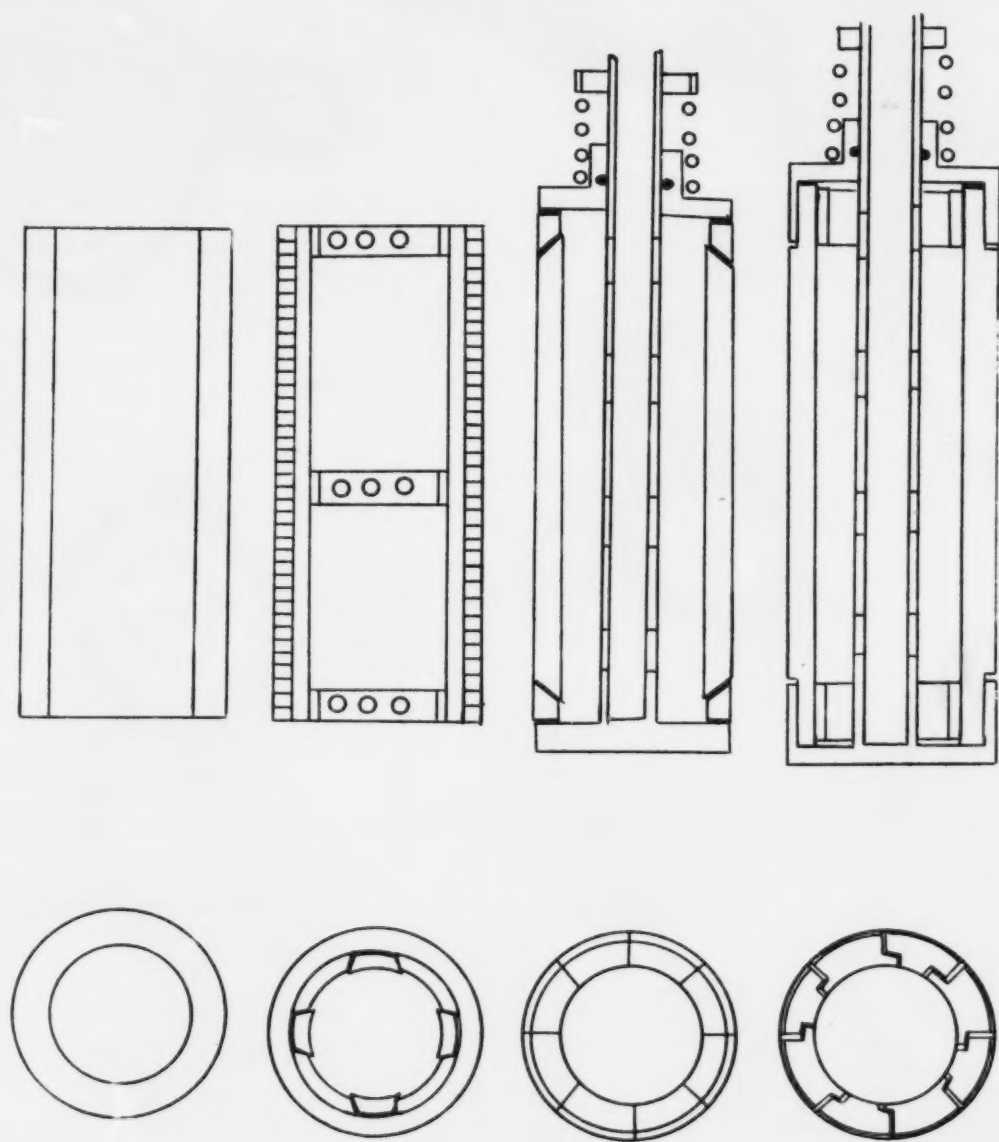


Figure 3-8. Alternate Frit Configurations (Ref. 3-13)

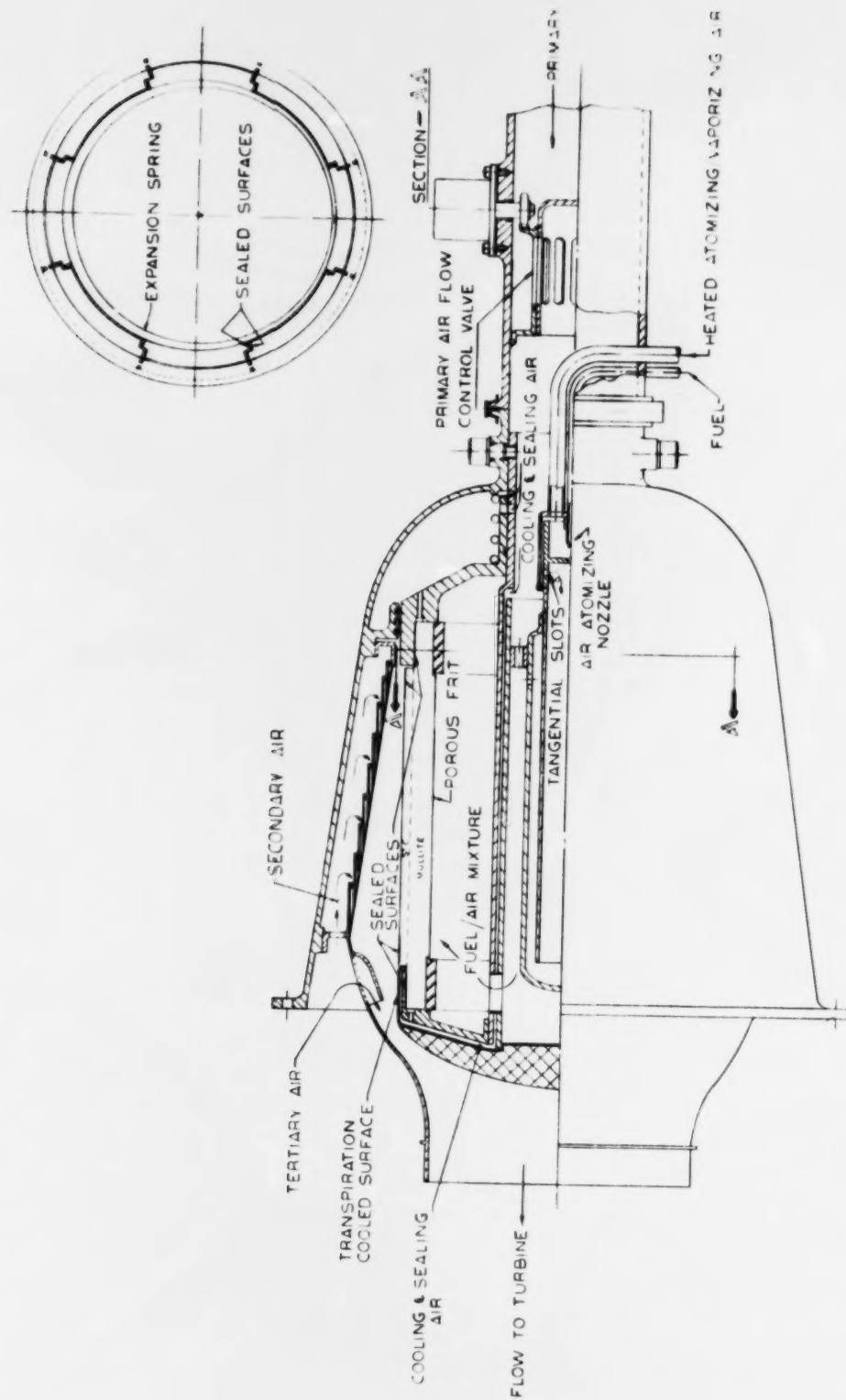


Figure 3-9. Porous Radiant Gas Turbine Combustor (Ref. 2-13)

nozzle. Spray from this nozzle is mixed with heated air issuing from tangential slots. This heated, rich fuel-air mixture passes down the central tube of the vaporizer and back up the surrounding annulus. It is then injected into the main primary air stream. To facilitate mixing, the latter stream issues in jets from orifices immediately upstream of the injection outlets of the vaporized rich mixture. The burner is sealed at its ends on axial faces which bear on the end support pieces. Cooling and sealing air is injected into the leakage paths across these surfaces in order to ensure that no fuel-air mixture bypasses the porous burner. On the downstream end, a transpiration-cooled surface on the burner support structure is employed where the effluent combustion gas passes over this structure. Tertiary air baffles are employed downstream of the primary combustion gas and secondary dilution air mixing zone. The separation of secondary and tertiary air delays the reduction of the combustor outlet gas temperature to the final turbine inlet temperature value until sufficient time for CO combustion has elapsed. Heat is transferred from the flame to the porous burner, causing it to become an incandescent radiation source. From here, heat is radiated to the heat sink screen-baffle structure, through which is passed the secondary air from the regenerator. Upstream of the combustor is the primary air-flow control valve.

Combustor concepts have been also devised for use with Rankine cycles. In this approach, shown in Figure 3-10, combustion heat feedback from the flame is dissipated in part to a tubular heat exchanger imbedded in the porous matrix. Superheated vapor is produced in a second heat exchanger by means of heat exchange with the partially cooled combustion gases. Experimental burners for an automotive Rankine power plant have been fabricated from conductive copper and copper alloys.

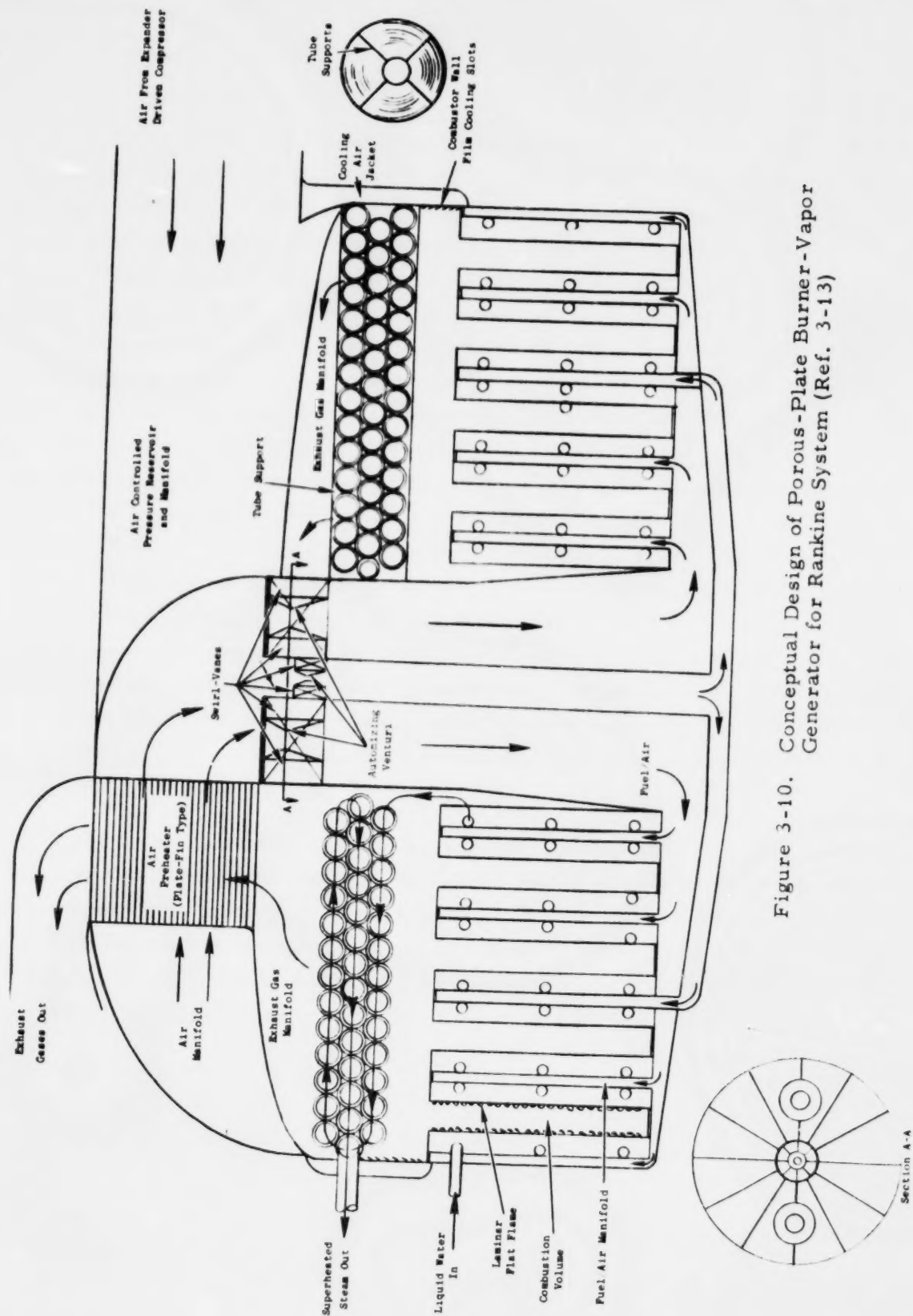


Figure 3-10. Conceptual Design of Porous-Plate Burner-Vapor Generator for Rankine System (Ref. 3-13)

3.2.4.2 Operational Characteristics

Limits characterizing burner behavior are expressed by General Electric in terms of the gas superficial (entrance) velocity into the burner, u_{25} (at 25°C) and the reciprocal absolute temperature of the products leaving the porous plate. At high superficial velocities, the flame zone becomes detached and insufficient heat feedback occurs; consequently, combustion can no longer be supported. As shown in Figure 3-11, this point represents the liftoff limit. A minimum velocity is required for stability at low heat release rates.

For the experimental work, superficial gas velocities have ranged between 4 and 50 cm/sec. Fuel-air equivalence ratios have ranged between 0.7 and 1.0, with some more recent data at approximately 1.1 using gasoline. As shown in Figures 3-12 and 3-13, heat feedback into the burner varies with superficial velocity, fuel type, and operating pressure. Maximum turndown ratios of about 7:1 have been achieved by General Electric with single burners operated with propane, and higher overall turndown ratios might be feasible with combustor staging.

The most difficult task has been to find a matrix material that will maintain its integrity and give satisfactory operating life. Cracking has been a problem with ceramic materials, and overheating and formation of local hot spots have occurred in the metallic configurations. Operation at elevated pressures has resulted in excessive surface temperatures. Surface oxidation also appears to be a materials problem which is being carefully addressed.

To assure complete fuel vaporization and mixing, which is deemed essential for proper combustor operation, General Electric has developed an air-driven acoustic fuel atomizer, shown in Figure 3-14, combined with an advanced small-volume tangential mixing chamber. With this design, General Electric feels that flashback, which represents a potential problem in all premixed and prevaporized systems, can be avoided. To date, flashback has not been encountered in any of General Electric's tests.

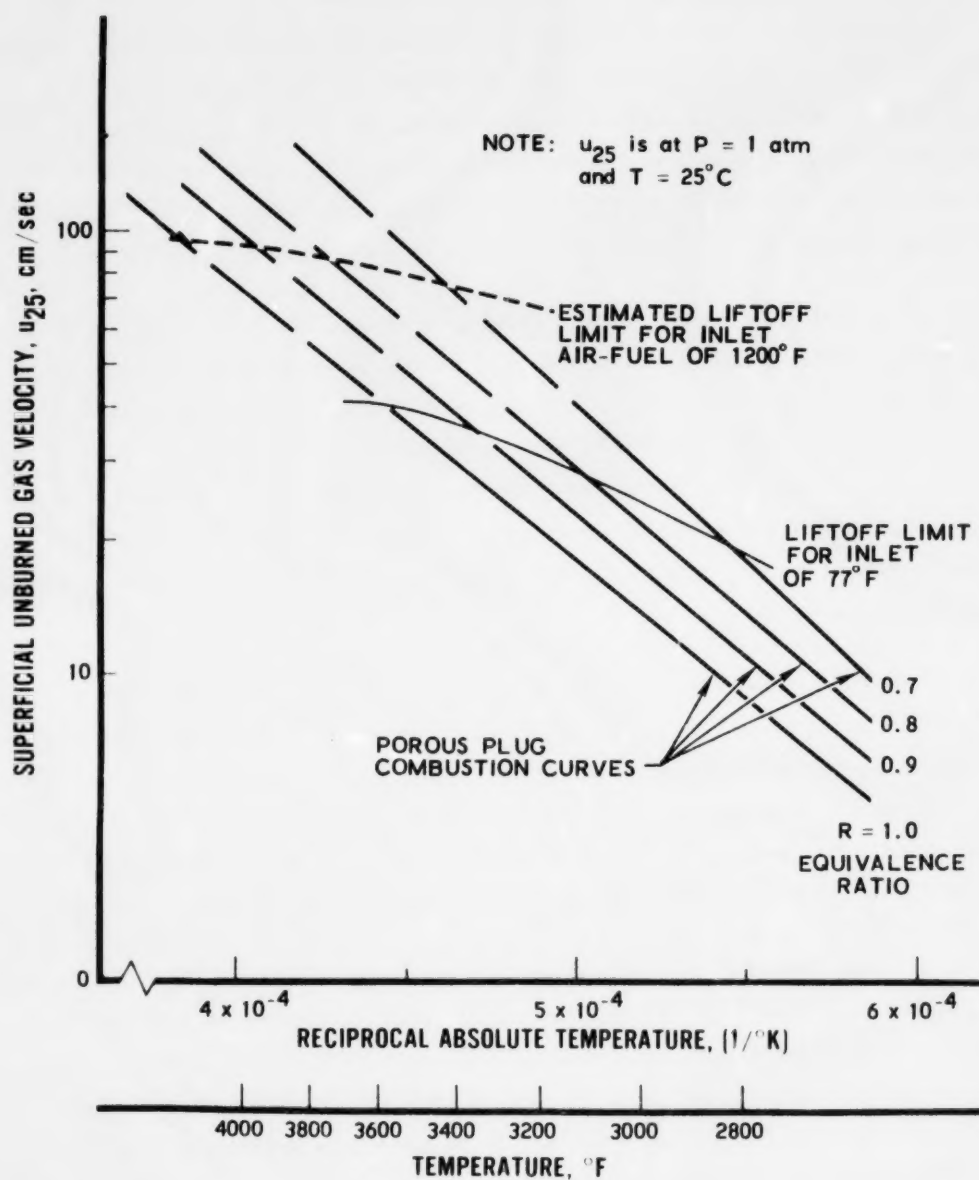


Figure 3-11. Effect of Unburned Gas Superficial Velocity and Equivalence Ratio Upon Flame Temperature (Ref. 3-13)

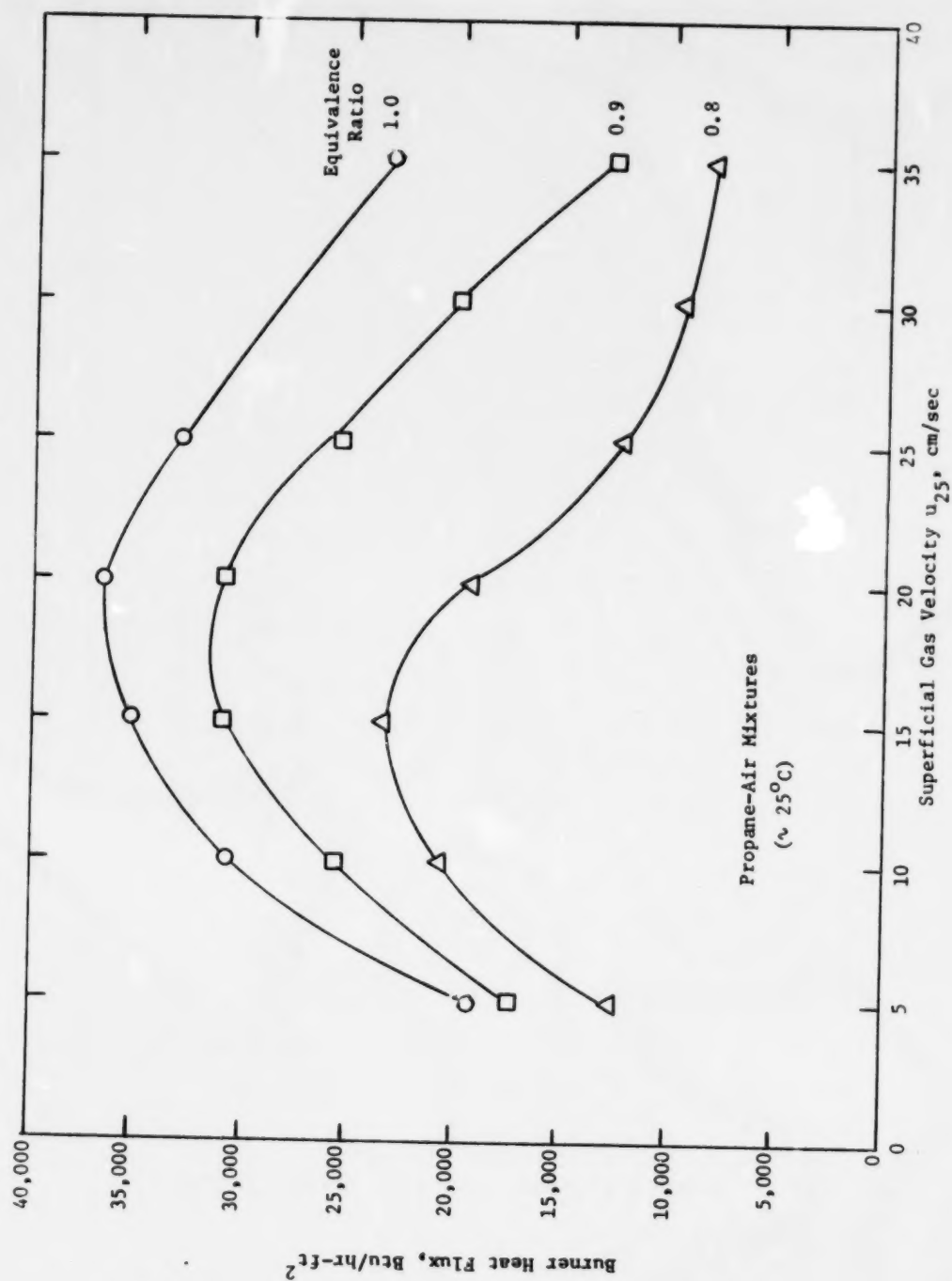


Figure 3-12. Heat Flux Back to the Burner for Propane-Air Mixtures (Ref. 3-13)

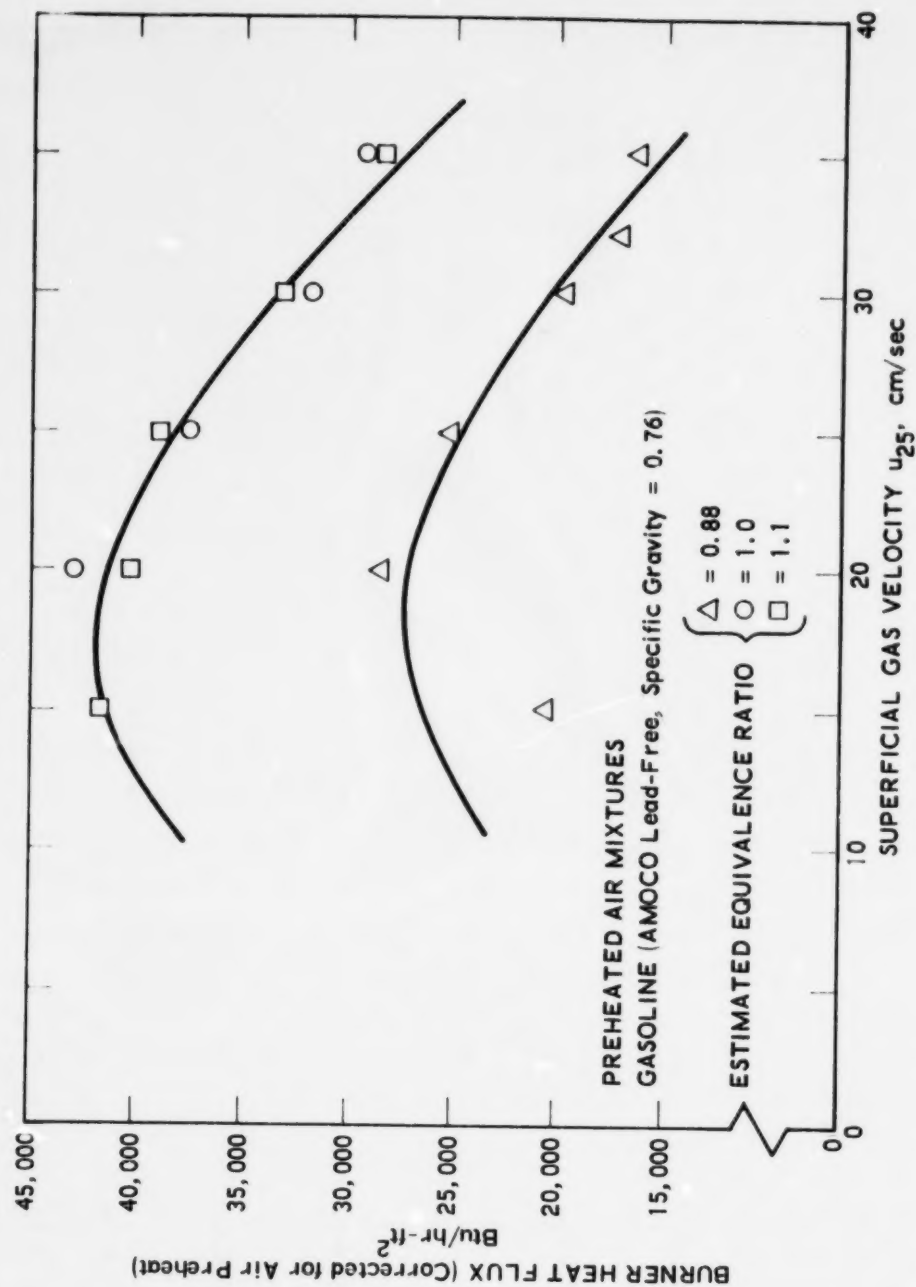


Figure 3-13. Heat Flux Back to the Burner for Gasoline-Air Mixtures (Ref. 3-13)

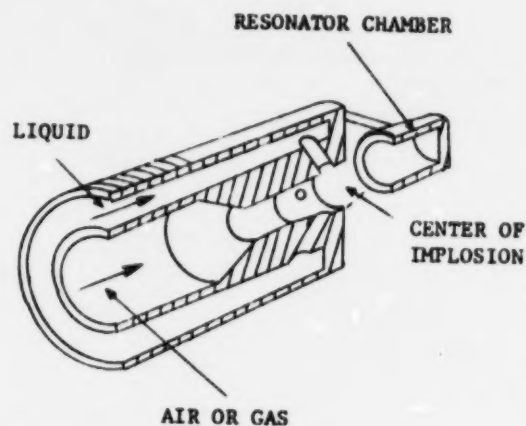


Figure 3-14. "Sonicore" Fuel Atomizer (Ref. 3-13)

3.2.4.3 Emission Characteristics

The porous plate combustors developed by General Electric for use in gas turbine and Rankine cycle engines are designed to meet the 1976 Federal Emission Standards for light-duty vehicles. As indicated in Figure 3-15, the NO_x emission index equivalent to the 1976 standards (assuming a fuel economy of 10 miles per gallon) has been achieved when operating the Rankine engine burner at 1 atm with propane as test fuel (equivalence ratio 0.9). In this particular test series, the CO standard was met for superficial gas velocities below about 25 cm/sec. No data were provided by General Electric for higher operating pressures. With prevaporized liquid fuels, General Electric obtained significantly higher NO_x emissions, even after accounting for the conversion to NO of the fuel bound nitrogen.

3.2.5 Selas Corporation of America

The Selas Corporation manufactures a variety of industrial furnaces and "radiant cup" burners which are used by various metal, glass, chemical, and petroleum processors. A significant part of Selas' technical capability

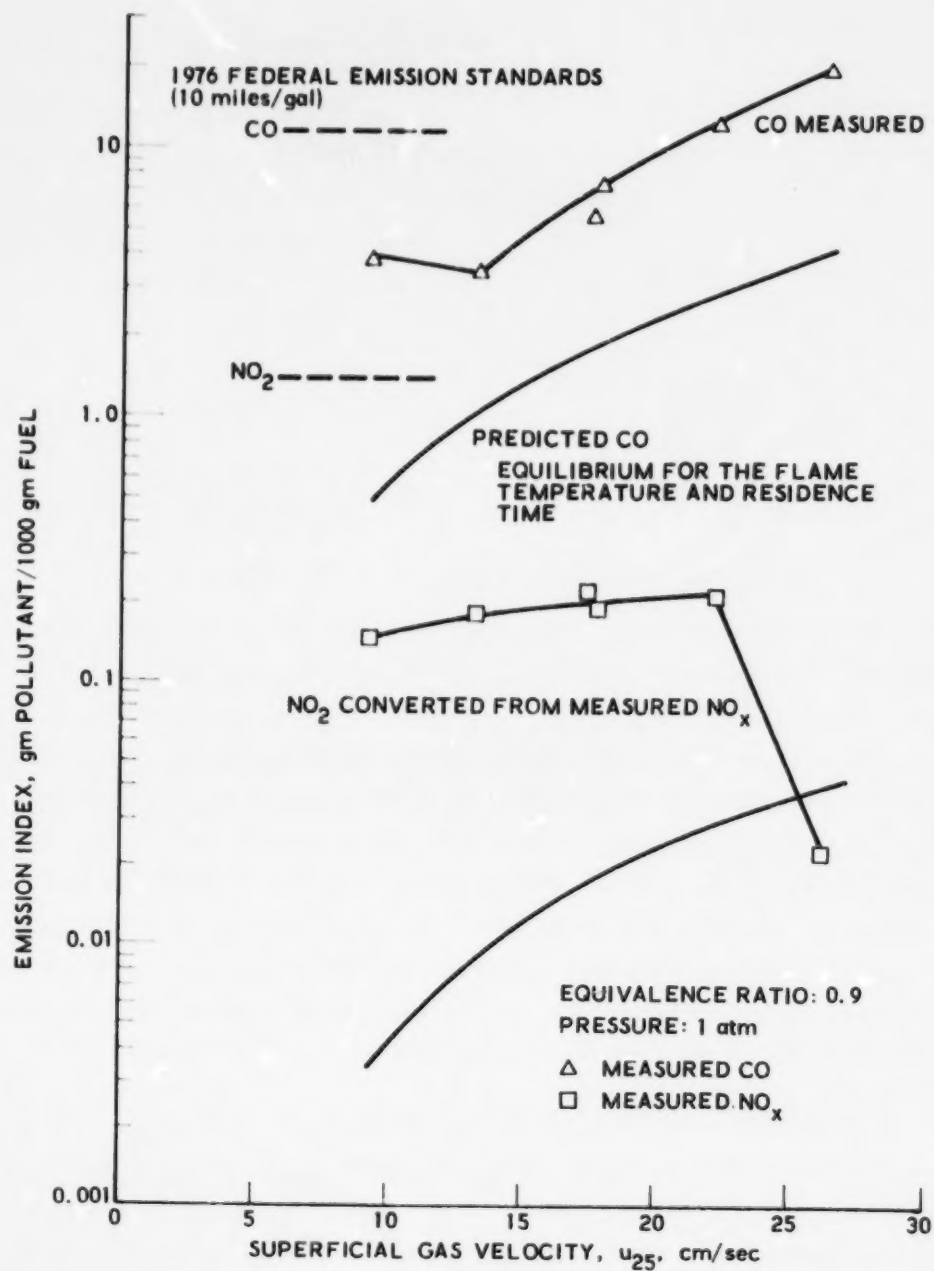


Figure 3-15. Preliminary Emission Measurements (Not Corrected for Water Content) (Ref. 3-12)

involves manufacture and assembly of industrial pyrolysis furnaces wherein hydrocarbon feedstocks are catalytically or thermally converted (cracked) to commercial by-products. Typical process fluid outlet temperatures vary between 1400°F and 1800°F, with pressures up to 500 psi. These units are horizontal or vertical tube furnaces containing a number of radiant-cup burners which are designed to provide precise and uniform control of the combustion gas composition and heat flux density patterns along the furnace profile (Ref. 3-14).

3.2.5.1 Combustor Design Features

Selas burners are procured and operated either as nozzle mix, premix, or aspirator configurations, depending upon the fuel type and the application. The feature which is common to Selas burners is that the combustible fuel-air mixture is introduced at a centrally located burner tip and forced to flow radially across the surface of a parabolic-shaped refractory cup where ignition and combustion occur. The general outline of a typical radiant-cup, gas-fired burner is shown in Figure 3-16.

Selas manufactures a line of gas or naptha (kerosene)-fired radiant burners, the largest being rated at about 2×10^6 Btu/hr. This particular unit has a diameter of 12 inches.

3.2.5.2 Operational Characteristics

In steady-state operation, as the mixture flows along the contour of the cup, rapid heat exchange occurs along the surface, enabling the cup to act as a radiative source. This is coupled with an internal recirculation flow pattern. Theoretically, the combustion is completed within the cup envelope. Thus, the need for additional or excess secondary air to complete the combustion process, as common with more conventional burners, is claimed to be unnecessary.

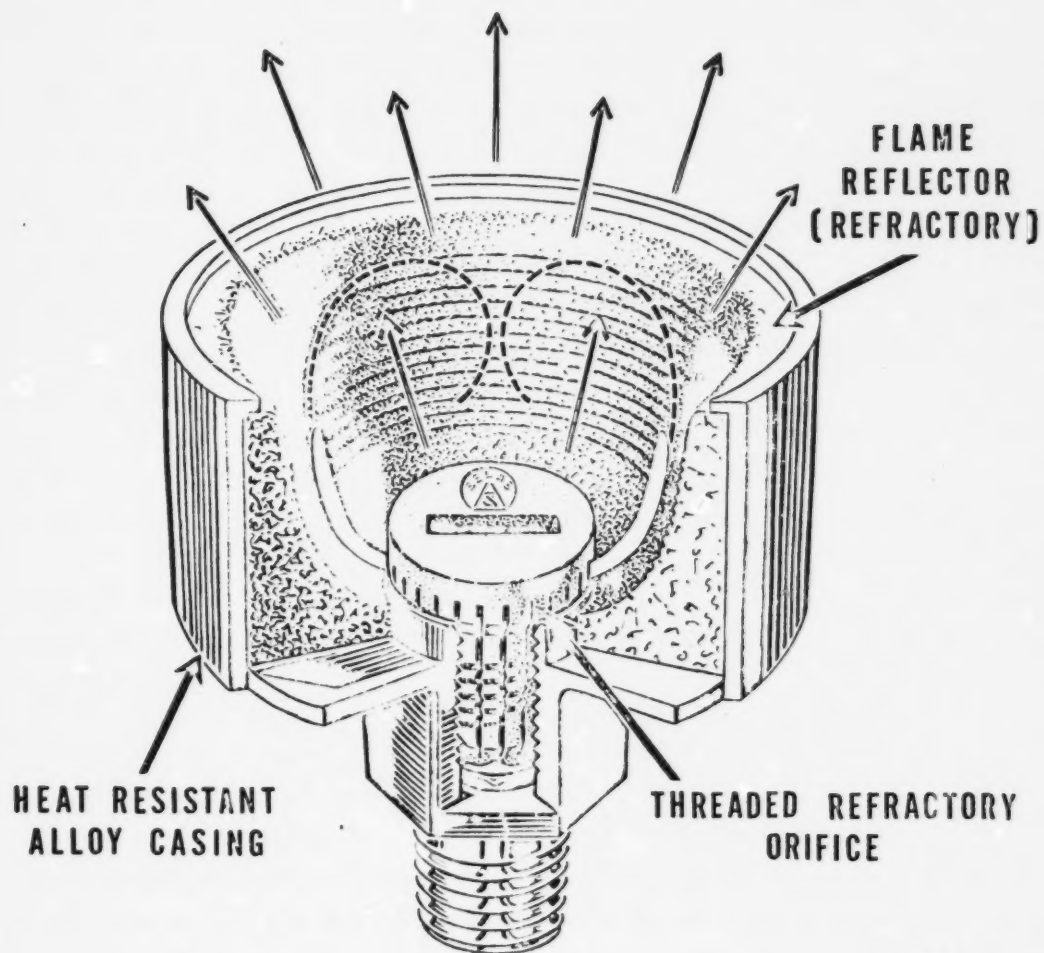


Figure 3-16. Typical Selas Radiant-Cup Air-Gas Burner

These burners, which are designed for a variety of gaseous fuels, can operate continuously with little or no maintenance. Special vortex-type configurations are available, which enable safe operation with high hydrogen-content gases often available to refineries. The nominal turndown ratio for most Selas production burners is between 5:1 and 10:1. Variable area burners also are available for larger turndown ranges. Oil-fired burners are not in production.

Occasional breakage of ceramic burner tips (not cups) necessitates replacement. Burners are designed to permit such replacement from outside the furnace wall after the individual fuel supply is shut off. However, the furnace remains operational during the replacement procedure.

3.2.5.3 Heat Transfer Characteristics

The radiant cup is designed to offer controlled heat transmission by radiating energy in a symmetrical beam. This is considered important in industrial furnace units operating at high internal tubular heater temperatures and pressures. Selas states that the high degree of symmetrical heating obtained with these cup burners tends to minimize distortion and bowing of heater tubes. The furnaces are designed and rated for continuous operation over several years.

3.2.5.4 Emission Characteristics

Test data on commercial furnace units are not available. However, tests conducted by Selas on laboratory configurations indicate that radiant-cup burners produce lower NO_x emissions than conventional burners. According to Selas, this is due to the intimate contact between the burning gases and the cup surface, which permits a portion of the heat of combustion to be transferred into the cup--resulting in lower gas temperatures. Moreover, aerodynamic forces generated within the cup are thought to induce recirculation of cooler furnace gases and the combination of these effects rapidly quenches the NO_x formation process. The NO_x emissions of an aspirator-type laboratory furnace operated on natural gas near stoichiometric are shown in

Figure 3-17. As indicated, the NO_x varies between 30 and 80 ppm, depending upon the selected furnace gas temperature. According to Selas, comparable NO_x emissions were obtained with No. 2 fuel oil.

3.2.6 University of Wisconsin

An experimental program of graduate research on low nitric oxide burners was undertaken by Peters at the University of Wisconsin (Ref. 3-15). The investigation consisted of determining the degree of nitric oxide reduction that can be achieved by means of nonadiabatic combustion of propane-air mixtures on a cooled porous metal plate.

3.2.6.1 Combustor Design Features

A cutaway drawing of the combustor arrangement is shown in Figure 3-18. It is comprised of a gas mixer, a porous metal disc burner, and a main burner housing. The steel top plate which holds the replaceable porous metal disc includes a water-cooling system for the porous disc. The main burner

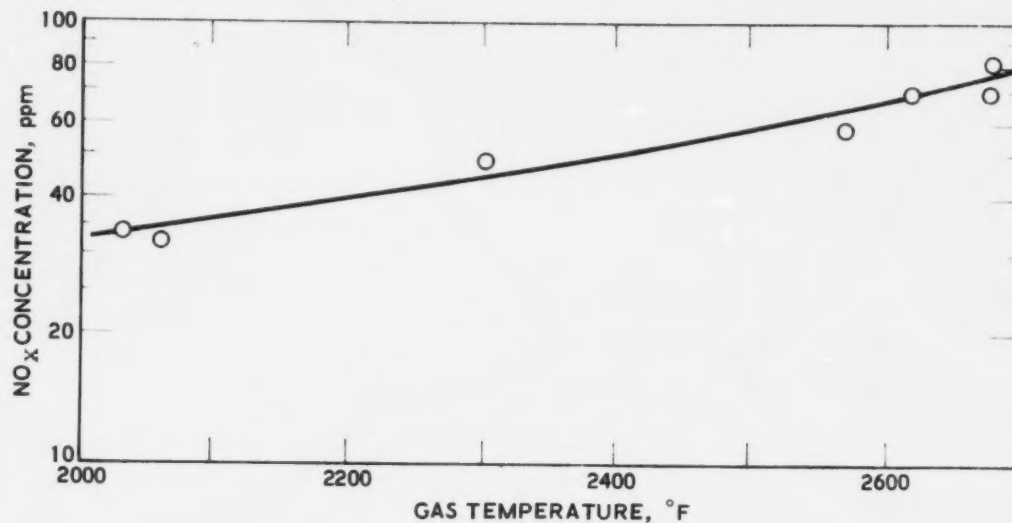


Figure 3-17. NO_x vs Gas Temperature for a Selas Inspirator Burner

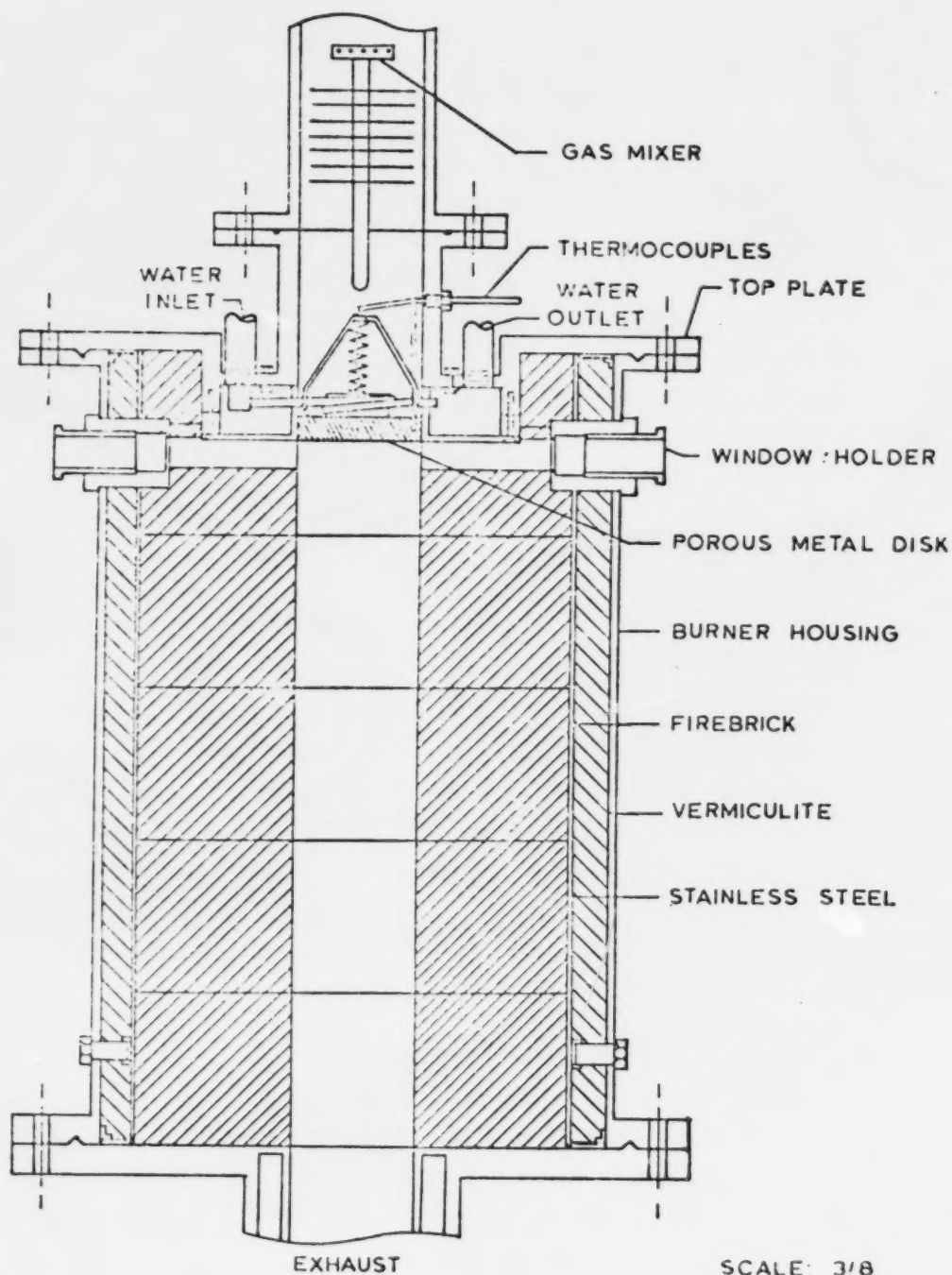


Figure 3-18. University of Wisconsin Burner Test Section
(Ref. 3-15)

housing is insulated and includes windows, igniters, gas sample probes, and thermocouples used for flame observation and monitoring of the combustion products.

Three types of porous disc materials were utilized in the program, including grades 340 and 460 of oilite filter material manufactured by the Amplex Division of Chrysler Corporation, and 70-micron rated P/N S-2121 sintered 316 stainless steel manufactured by the Sintered Specialties Division of Parker Pen Corporation. All the discs were 2.0 inches in diameter and either 0.25, 0.38, or 0.50 inch thick.

A schematic of the combustor test setup is presented in Figure 3-19, showing the main components of the air and fuel supply systems. The air is provided by a compressed air source, and the air flow rate is measured with an orifice meter. The "natural grade" propane fuel used in the program is supplied from a tank and controlled by a single-stage regulator. From the regulator, the fuel is routed into a filter with a liquid separator and then through a rotameter to measure the flow rate. Following the rotameter, the fuel passes through a needle valve and into the gas mixer located upstream of the burner inlet section. Ideally, the mixer delivers a homogeneous, premixed propane-air mixture to the burner. The combustible mixture then flows through a water-cooled, sintered porous metal disc and is ignited on the back side of the disc. The combustion products pass through an insulated tube, where gas samples are taken, and finally into an exhaust system.

In the test program, the combustor was operated at fuel-air equivalence ratios between about 0.7 and 1.2, pressure levels of 19.3, 39.9, and 54.3 psia, and a mixture inlet temperature of 530°R. The mass flow rate through the burner was varied. For example, at 39.9 psia pressure, the flow rates covered the range between 3.3 lb/hr and 30.6 lb/hr. Smaller flow variations were considered for the other operating pressures.

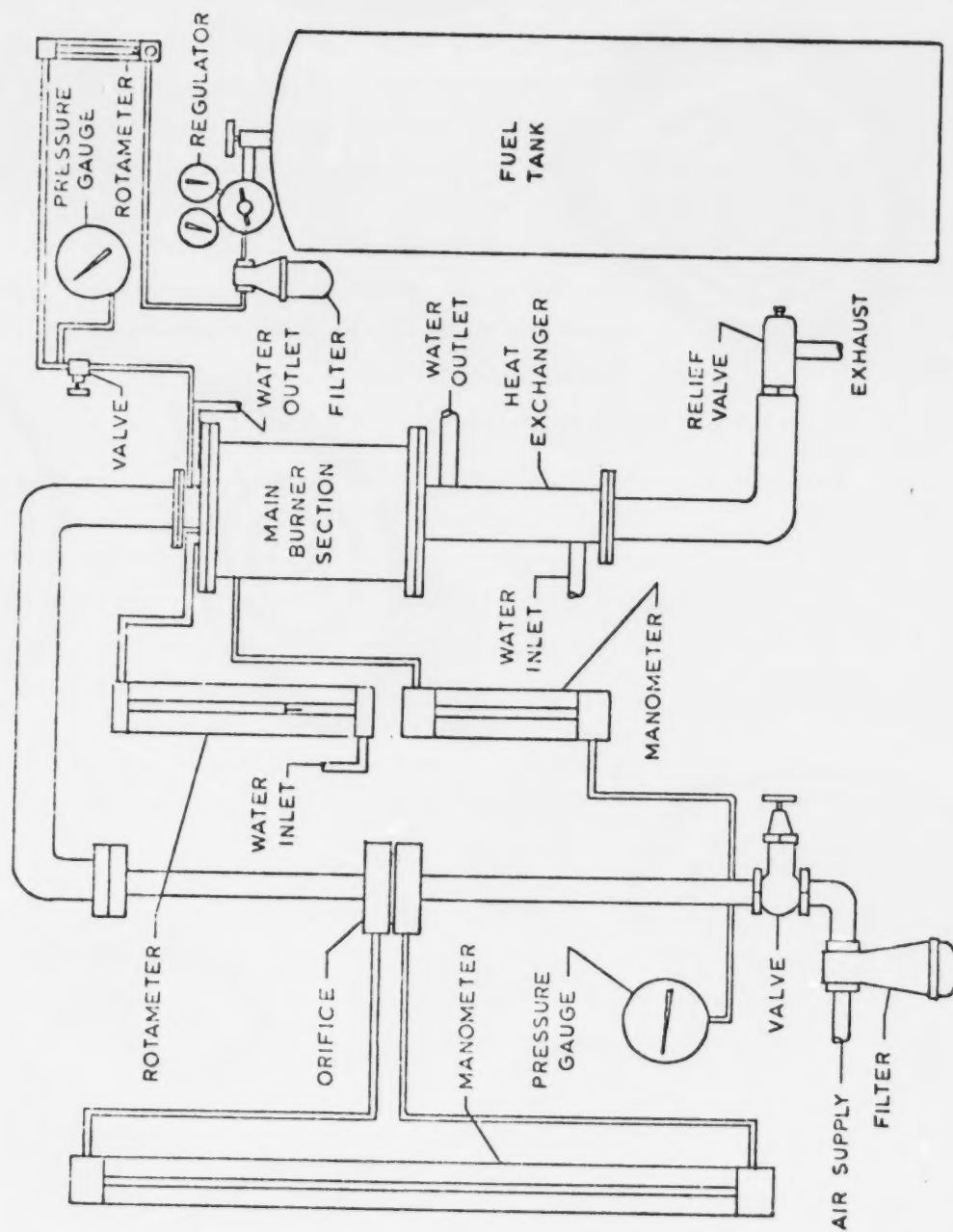


Figure 3-19. University of Wisconsin Fuel and Air Inlet System (Ref. 3-15)

3.2.6.2 Heat Transfer Characteristics

In the test program, the fraction of the heat of combustion returned to the porous plate was varied by controlling the mixture equivalence ratio and the burner mass flow rate, as shown in Figure 3-20, for an operating pressure of 39.9 psia. The heat flux reaches a maximum at equivalence ratios slightly higher than stoichiometric and generally increases with decreasing flow rate. These trends are in agreement with the results obtained by General Electric and others. As indicated in the figure, as much as 30 percent of the combustion heat can be transferred to the cooled porous disc. Similar results were obtained for the other operating pressures.

3.2.6.3 Emission Characteristics

The nitric oxide emissions measured at an operating pressure of 39.9 psia and a residence time of 40 msec are plotted in Figure 3-21 as a function of fuel-air equivalence ratio and mixture flow rate. As expected, the NO concentrations are very low at low equivalence ratios, especially at low flow rates, reflecting the lower temperatures of the combustion products at these operating conditions. The NO_x emissions increase with increasing equivalence ratio, reaching a maximum near stoichiometric. Also shown in Figure 3-21 are the computed adiabatic equilibrium NO_x concentrations. In the lean regime, the NO_x emissions with flame cooling are substantially lower than the corresponding equilibrium values.

Small variations in the measured NO_x emission levels were observed for the three different porous-plate configurations evaluated in the program. These differences are attributed to the variations in plate thickness, thermal conductivity of the material, and contact resistance around the circumference of the discs.

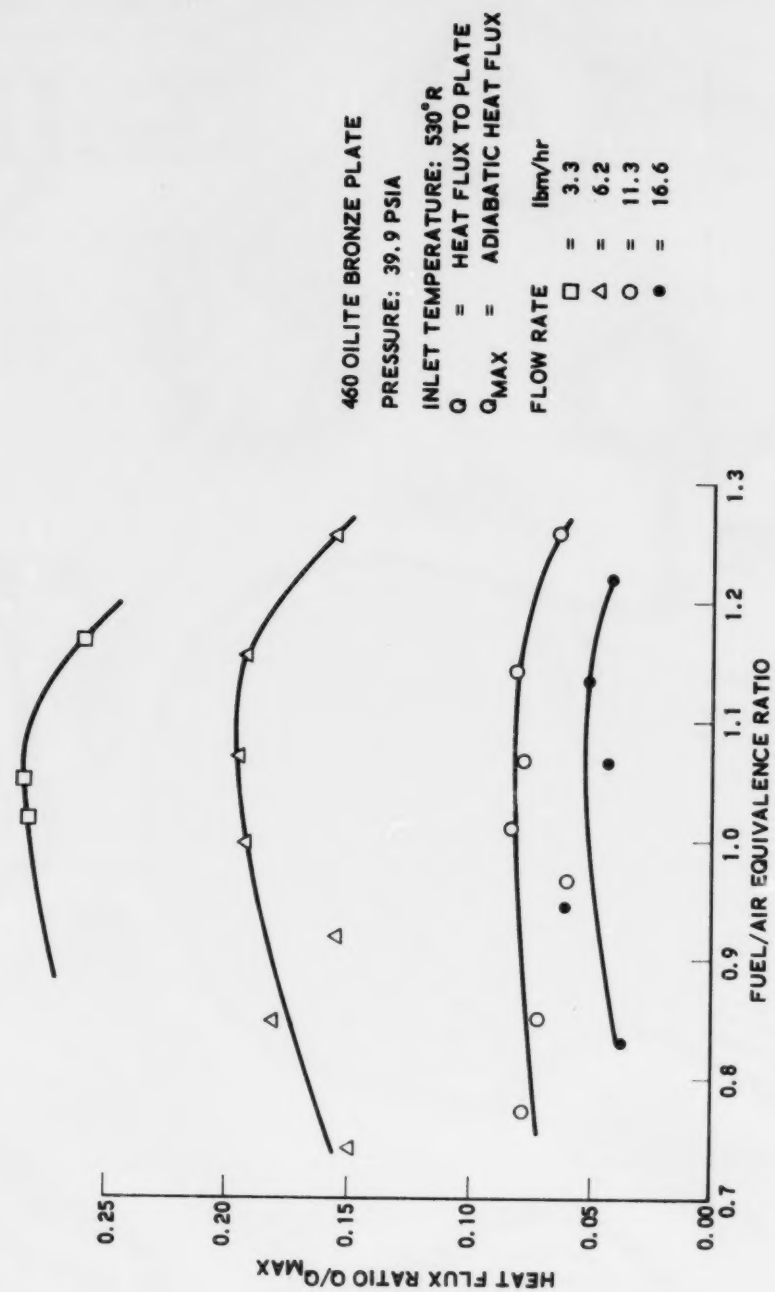


Figure 3-20. Q/Q_{max} vs Equivalence Ratio Profiles for Various Mass Flow Rates (Ref. 3-15)

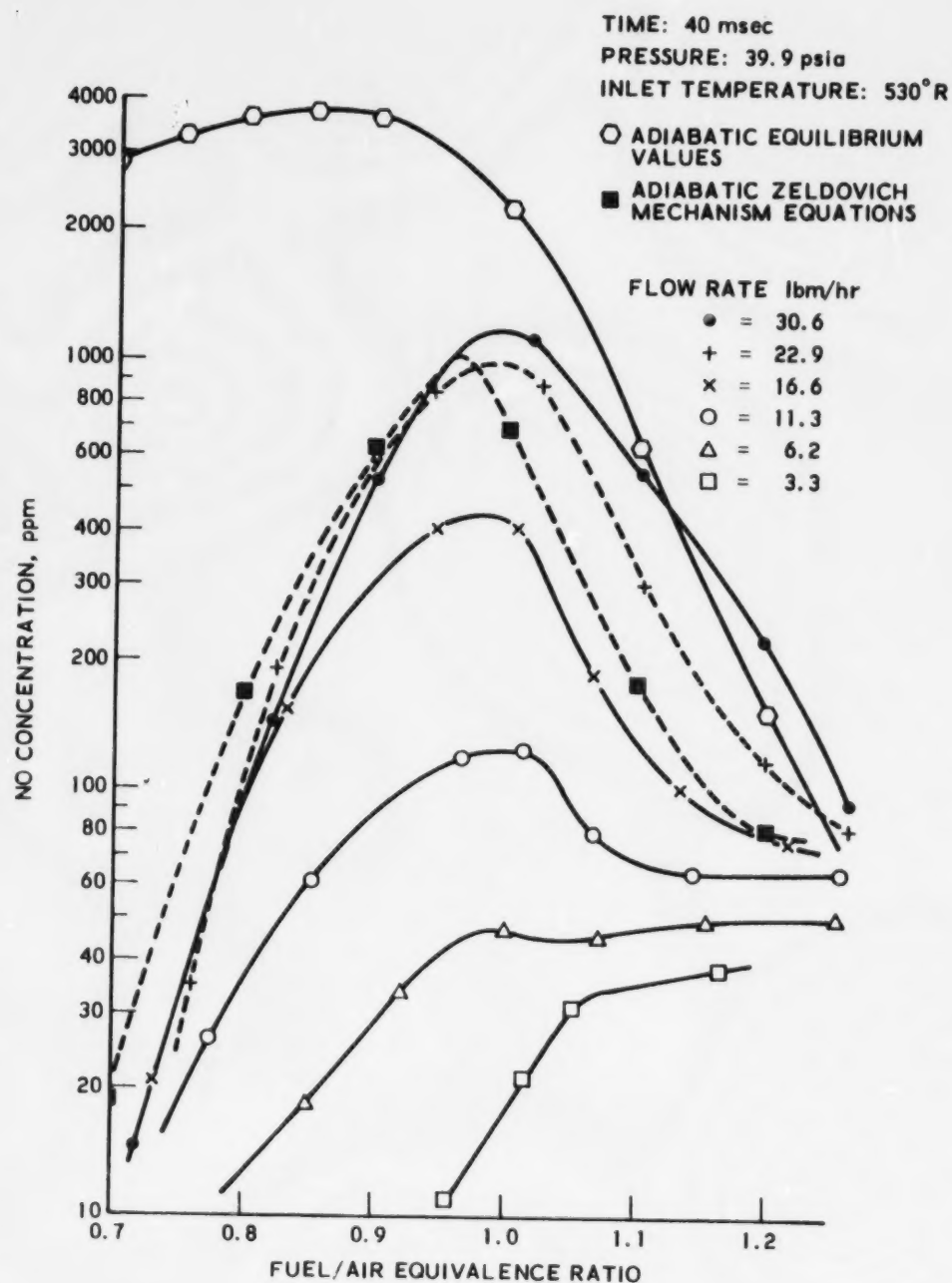


Figure 3-21. NO vs Equivalence Ratio Profiles for Various Mass Flow Rates (Ref. 3-15)

The CO emissions from these burners were very low and in reasonable agreement with the equilibrium values computed for the particular fuel-air equivalence ratios, indicating good combustion efficiency under all operating conditions.

Except for a few isolated cases, the observed hydrocarbon emissions were less than 10 ppm hexane. According to Peters (Ref. 3-15), the experimental accuracy was probably no better than ± 10 ppm.

3.2.7 Other Organizations

Several other organizations are involved in the development and/or manufacture of heterogeneous (radiant) combustion devices, including AiResearch, Holden, Institute of Gas Technology, and Perfection. The information provided by these companies is briefly discussed in the following sections.

3.2.7.1 AiResearch Manufacturing Company

Porous-plate combustors/heaters are currently being studied for potential use in closed Brayton cycle (gas turbine) engines. Emission test data with propane fuel indicate HC, CO, and NO_x emission levels of about 10 ppm or less, at an equivalence ratio of 0.8. Diesel fuel data gave slightly higher emissions (Ref. 3-16).

3.2.7.2 A. F. Holden Company

This company manufactures porous refractory blocks and "luminous wall" furnaces for various industrial heating and metal treatment applications. Allowable maximum wall temperatures of 2000°F and above have been maintained in certain applications. The refractory brick can be operated over a range of fuel-air equivalence ratios, but operation near stoichiometric is preferred. Maximum heat input is about $150,000 \text{ Btu/hr-ft}^2$. Currently, these burners are used only with gaseous fuels, but certain liquid fuels might be acceptable as well. A minimum gas flow rate of $200 \text{ ft}^3/\text{hr-ft}^2$ is required to cool the brick and prevent flashback. Emission data are not available for these burners (Ref. 3-17).

3.2.7.3

Institute of Gas Technology

This organization has recently completed a study for NASA/Lewis relating to emissions from porous-plate combustors designed for use in closed Brayton cycle (gas turbine) systems. The surface combustor considered for this application is schematically shown in Figure 3-22 (Ref. 3-18). Based on this study the Institute of Gas Technology concludes that porous-plate burners

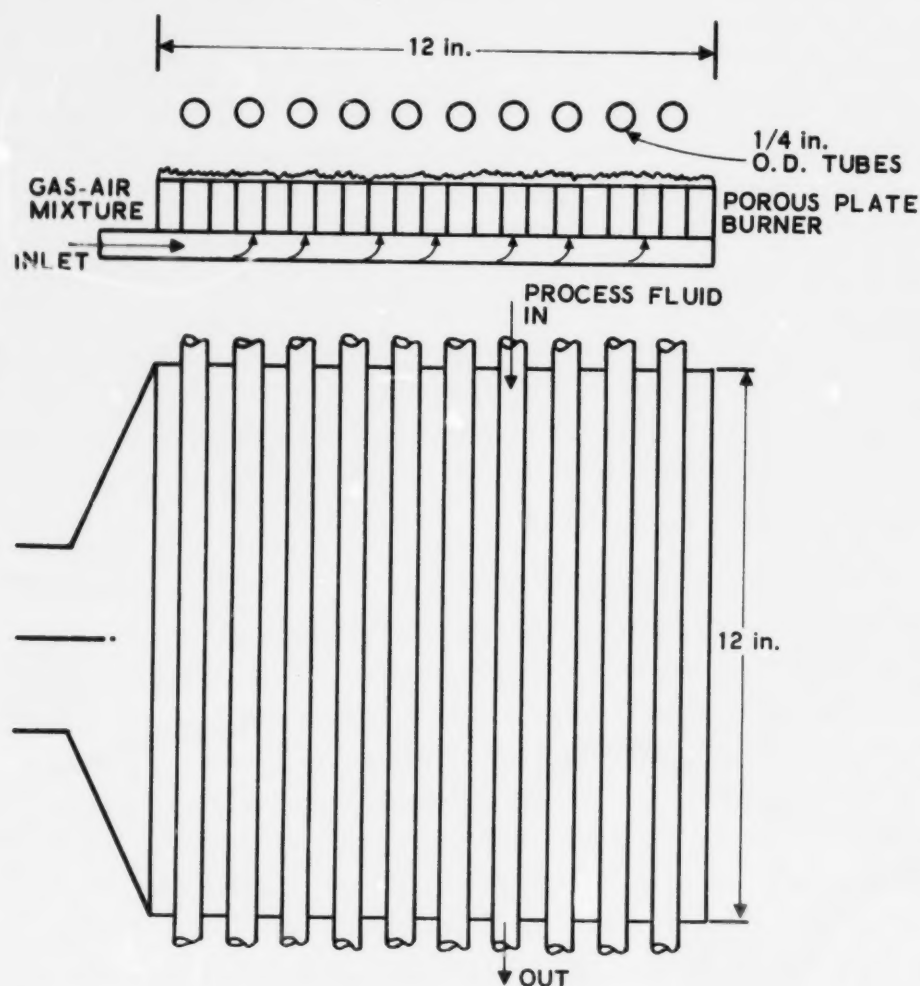


Figure 3-22. Surface Burner Geometry (Ref. 3-18)

fabricated from high-conductivity materials having a fine pore structure (consistent with allowable pressure drops) provide a practical approach to a low-emission combustion system, provided the plate temperature is kept low and the flame is quenched rapidly. Potential problem areas cited by the institute include overheating of the plate at high heat loadings, and flame front instability.

3.2.7.4 Perfection Products Company

Perfection manufactures a line of flow-through gas-flame radiant burners for use in industrial space heaters, food processing, drying ovens, and other uses. Emphasis is on operating safety and burner lifetime, which is measured in years. High radiation efficiency is achieved with its newly developed waffle-face silicon carbide burner tile which has a maximum temperature capability of 1850°F. Total design heat release rates of these burners are below 100,000 Btu/hr-ft². Operation of the burners at near-stoichiometric conditions results in CO emissions of about 300 to 400 ppm. Data on NO emissions are not available.

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SECTION 4

STATE-OF-THE-ART REVIEW OF CATALYTIC DEVICES

4.1

INTRODUCTION

The discussion of catalytic combustion devices presented in the following sections is primarily based upon the technical information acquired from a number of organizations, including Engelhard Industries, NASA/Lewis, Air Force Aero Propulsion Laboratory (AFAPL), and the Environmental Protection Agency (EPA), and on supplementary information extracted from the open literature.

With the exception of a small number of exploratory tests conducted by Engelhard and the Combustion Research Section, Control Systems Laboratory of the EPA, there is no information available at this time regarding the performance characteristics of high-temperature catalytic combustors of potential interest to stationary gas turbine and power plant applications. However, a considerable amount of experience has been gained from the development and operation of catalytic converters used in many industrial processes, as well as the exhaust treatment of automotive engines under a variety of operating conditions. In particular, the effects of catalyst deactivation due to poisoning and high-temperature operation on the lightoff characteristics and the service life of these systems have been evaluated by the automotive and chemical process industries. Since catalytic combustors are likely to have design features similar to those of industrial and automotive catalytic devices, and since they are expected to be influenced by the same factors affecting performance and durability, a brief discussion of these parameters is considered appropriate.

The design features of base metal, platinum-group metal, and nonmetallic catalysts--supported on monolithic, pellet, and fibrous pad substrates--are examined in Section 4.2, followed by a section on catalyst performance degradation due to poisoning, overtemperature conditions, and vibratory

loads. Section 4.4 discusses the operational characteristics of four different catalytic system configurations. These include automotive oxidation catalysts, industrial tail gas abatement catalysts, low-temperature catalytic heaters, and, finally, the high-temperature catalytic combustors currently considered by several organizations for potential application in mobile and stationary gas turbines.

4.2 CATALYST FEATURES

4.2.1 Catalytic Process

In chemical reactions, the molecules of the reactants are required to overcome specific potential energy barriers (Ref. 4-1). The rate of a reaction, which is determined by the number of molecules having sufficient kinetic energy, can be increased by (1) increasing the temperature of the reactants, and (2) incorporating a suitable catalyst. In the case of the catalyst, the chemical reaction proceeds in the following manner. The reactants are initially brought into contact with the catalyst surface by diffusion. Upon contact, the catalyst reacts with the molecules of the reactants to create an unstable intermediate product, which effectively lowers the energy barrier between the molecules involved in the reaction. The intermediate product reacts further at the catalyst surface and forms the final product, which is then removed from the surface of the catalyst by means of desorption and diffusion. Under ideal operating conditions, the catalyst remains unchanged in the reaction process. Its only function is to promote the chemical reactions which would otherwise not occur or occur very slowly.

4.2.2 Catalyst Requirements

Necessary attributes for catalytic devices include adequate chemical activity, selectivity, and service life. In addition, the catalyst substrate must be capable of withstanding the mechanical and thermal loads generated in the particular duty cycles.

The activity of the catalyst under normal operating conditions has a bearing on the size of the catalytic unit required for each application. Also, high activity at low temperatures is desirable in order to minimize the amount of

reactant preheating needed for catalyst lightoff. Table 4-1 presents the lightoff temperature for a number of catalysts with respect to nitrous oxide decomposition (Ref. 4-2).

Selectivity represents another important parameter. Frequently, different reaction products can be obtained from a given set of reactants, depending upon the composition of the catalyst used in the process. For example, in ammonia oxidation, either nitric oxide and water or nitrogen and water can be formed. The yield of nitric oxide can be increased simply by increasing the rhodium content in the platinum base catalyst normally utilized in the ammonia oxidation process (Ref. 4-3).

Catalyst life is a most important aspect, particularly in the case of costly noble metal designs. Short life requires frequent replacement of the catalyst and this results in higher overall process cost. For these reasons, industrial catalysts are generally designed for several thousand hours of maintenance-free operation.

Table 4-1. Catalyst Lightoff Temperature--
Decomposition of Nitrous Oxide

Catalyst	Lightoff Temperature, °C
Cu_2O	215
CoO	225
NiO	300
CuO	380
MgO	390
CaO	420
CeO_2	450
Al_2O_3	480
ZnO	600
CdO	615
Cr_2O_3	660
Fe_2O_3	700

4.2.3 Typical Catalysts

Literally thousands of different catalyst materials and formulations have been evaluated over the years for potential use in a variety of chemical processes and automotive exhaust treatment systems. These configurations fall into three basic categories: platinum group metal catalysts, base metal and promoted base metal catalysts, and nonmetallic catalysts. In general, the metallic catalyst materials are deposited on a suitable substrate. A number of different deposition methods have been developed, including precipitation, electroplating, coating with a paste, deposition of colloidal materials, and impregnation of the substrate with a salt solution.

4.2.3.1 Platinum Group Metal Catalysts

The platinum group metals, especially platinum, palladium, and rhodium, are being used extensively in industrial catalysts, either by themselves or in the form of alloys. As indicated in Ref. 4-4, palladium is the most effective noble metal catalyst for many processes, followed by platinum and rhodium. This is illustrated in Table 4-2, showing the relative reaction rates for catalytic oxidation of methane for a platinum and a palladium catalyst supported on γ -alumina (Ref. 4-5). As indicated, the reaction rates obtained with palladium are substantially higher than those for platinum. Noble metal catalysts are used primarily in oxidation processes such as nitric acid manufacture, tail gas abatement, and automotive exhaust emission control.

Table 4-2. Relative Reaction Rates--Catalytic Oxidation of Methane

Catalyst/Substrate	Activation Energy kcal/mole	Reaction Rates Relative to that of Palladium/ γ -Alumina at 400°C			
		400°C	450°C	600°C	800°C
Palladium/ γ -Alumina	19.6	1.0	2.76	28.7	235.9
Platinum/ γ -Alumina	9.2	0.44	0.71	2.1	5.7

A number of the platinum group catalysts tested by the automotive industry are listed in Table 4-3. The HC and CO conversion efficiency of these catalysts and the test conditions are also listed in this table (Ref. 4-6).

4.2.3.2 Base Metal Catalysts

Base metal catalysts employ metals or oxides of metals from the transitional group of the periodic table of elements, including vanadium, chromium, manganese, iron, cobalt, nickel, copper, and zinc. These catalysts are used primarily by the chemical and petroleum industries in a variety of processes such as hydrogenation, ammonia synthesis, methanol synthesis, and oxidation reactions. A number of typical catalyst configurations used in these applications are listed in Table 4-4 (Ref. 4-2).

Generally, several metals and their oxides are combined to increase the effectiveness of the catalyst compared with single component configurations. For instance, in the synthesis of methanol from carbon monoxide and hydrogen, mixtures of zinc oxide and chromium oxide are used extensively. As illustrated in Figure 4-1, neither of these oxides is very effective by itself. However, by adding about 20 to 40 percent chromium oxide to the zinc oxide, the efficiency of the process increases substantially (Ref. 4-2). In this case, chromic oxide acts as a promoter whose principal function is to minimize the crystallite size of the catalyst. There is ample evidence that the effectiveness of catalysts increases as the size of the crystallites is reduced.

A number of automobile and catalyst manufacturers are experimenting with promoted base metal catalyst formulations containing small amounts of platinum group metals for potential use in automotive emission control systems. These efforts are aimed primarily at the development of a less expensive catalyst that approaches the performance of noble metal designs. Platinum and palladium appear to be likely promoter choices (Ref. 4-7). Table 4-5 presents a small fraction of the base metal catalyst formulations tested by the automotive industry. Also listed in this table are the pollutant concentrations at the inlet of the catalyst, catalyst efficiency, and operating temperature (Ref. 4-8).

Table 4-3. Catalytic Removal of HC and CO--Platinum Group Metal Automotive Catalysts

Catalyst Composition, % weight	Catalytic Conversion, ^a %		Test Conditions					Notes
	HC	CO	TEL, ^b ml/gal	Duration	Engine Type, cyl	Average Catalyst		
						Temperature, °C		
1Pd/1Pt/Al ₂ O ₃	83	76	2.7	188 hr	1	-	Air added to exhaust	
0.19Pt/(Ba)/Al ₂ O ₃	69	81	3	40 hr	8	435	Air added to exhaust	
0.19Pt/Al ₂ O ₃	92	81	3	-	-	-	Nonuniform distribution of Pt	
0.375Pt/0.5F/0.25Cl/Al ₂ O ₃	61	-	present	12,000 mi	8	-		
0.1Pt/0.5F/Al ₂ O ₃	93	80	4.8	-	8	-		
0.4PtAl ₂ O ₃	55	-	3	40 hr	-	-		
3.2Pd/Al ₂ O ₃	70	95	0.2	10,000 mi	8		Glass-fiber thread and fiber support; air added to exhaust	

^aAt end of test period
^bTEL: tetraethyl lead

^aAt end of test period

^bTEL: tetraethyl lead

Table 4-4. Base Metal Catalysts--Industrial Processes

Type of Reaction	Examples	Catalysts
Ammonia synthesis	$N_2 + 3H_2 \rightleftharpoons 2NH_3$	Iron, molybdenum, osmium, uranium, etc. Promoted iron (K_2O , Al_2O_3)
Methanol synthesis	$CO + 2H_2 \rightleftharpoons CH_3OH$	Copper, zinc oxide Zinc oxide with chromia
Oxo-reaction	$CO + H_2 + RCH = CH_2 \rightarrow RCH_2 \cdot CH_2 \cdot CHO$	Cobalt + thoria
Hydrosulphurization	$RSH + H_2 \rightarrow RH + H_2S$	Cobalt-molybdena Iron and tungsten sulphides
Dehydration + dehydrogenation	$2C_2H_5OH \rightarrow CH_2 = CH \cdot CH = CH_2 + 2H_2O + H_2$	Copper, Cu + Ni + Cr_2O_3
Oxidation	$SO_2 \rightarrow SO_3$ $CO \rightarrow CO_2$ $CO + H_2O \rightleftharpoons CO_2 + H_2$	Vanadium pentoxide (V_2O_5 , V_2O_4) Manganese dioxide (MnO_2 , Mn_2O_3) Iron (Fe, Fe_3O_4)
Halogenation - dehalogenation	$4HCl + O_2 \rightleftharpoons 2Cl_2 + 2H_2O$ $RH + O_2 + HCl \rightleftharpoons RCl + H_2O$ $RH + Cl_2 \rightarrow RCl + HCl$	Chlorides of copper, zinc, or mercury on carriers Chlorides of copper, zinc, or mercury on carriers Chlorides of copper or silver on carriers
Exchange reactions	D_2 with H_2 or RH or NH_3 O with O in oxides, N_2O , H_2O	Transition metals Many oxides

Table 4-5. Catalytic Removal of HC and CO--Base Metal Automotive Catalysts

Catalyst Composition, Percent Weight	Exhaust Gas Composition Before Converter, ppm			Catalytic Conversion, Efficiency, Percent ^a			Test Conditions				Remarks
	HC	CO	NO _x	HC	CO	NO _x	IEL, ml/gal ^b	Duration, hr	Engine Type	Average Catalyst Temperature, °C	
MnO _x /CuO/NiO/CrO _x	-	-	310-630	80	>80	87-99	present	341	8 cyl	425-650	Air added for HC and CO conversion
NiO/Ba/Al ₂ O ₃	1,400	29,000	155	85	77	96	0	3	CFR ^c	485	
NiO/Ba/Al ₂ O ₃	-	-	-	39	45	98	3	120	CFR	-	
7CuO/0.04SiO ₂ /Al ₂ O ₃	325	10,000	-	83	95	-	3	100	CFR	-	Federal Test Cycle
3CuO/75SiO ₂	-	-	1,000	-	-	90	present	-	2 cyl	380	
6CuO/6Cr ₂ O ₃ /Al ₂ O ₃	418	-	-	54	-	-	present	350	8 cyl	-	Odorous exhaust subsequently removed by catalytic oxidation over 1 Pd/Al ₂ O ₃
CuO/Cr ₂ O ₃	20,000	60,000	4,000	88	95	-	present	-	8 cyl	285	O ₂ (7.3 vol %) added to exhaust
62CuO/5Co ₂ O ₃ /33Al ₂ O ₃	2,000	60,000	1,500	-	-	90	1.6	238	8 cyl	480	High thermal stability, high attrition resistance
8CuO/4Co ₂ O ₃ /1V ₂ O ₅ /Al ₂ O ₃	325	40,000	-	54	72	-	12	50	CFR	-	Federal Test Cycle
20CuO/0.1Ag ₂ O/Al ₂ O ₃	1,400	3,000	-	>80	>50	-	-	-	-	-	
6CuO/0.1Pd/6SiO ₂ /Al ₂ O ₃	140	1,750	-	76	58	-	3	-	CFR	510	Air added to exhaust
0.25-15CuO/0.05-0.3Pd/SiO ₂ /Al ₂ O ₃	-	-	-	69	90	-	12	60	CFR	-	0.12% S in fuel, multi-layer catalyst
5-10V ₂ O ₅ /Al ₂ O ₃	2,900	-	-	72	-	-	0	-	1 cyl	-	In presence of 3 TEL HC conv. = 30 vol %
50Co ₃ O ₄ /CaAl ₂ O ₄	12,000	60,000	-	77	63	-	present	600	1 cyl	-	
4-15 MnO _x /2-5Ti/Al ₂ O ₃	375	40,000	-	62	68	-	12	75	CFR	-	
4U ₃ O ₈ /Al ₂ O ₃	4,650	-	-	70	-	-	3	-	8 cyl	-	Air added to exhaust
MoO _x /Al ₂ O ₃	2,800	-	-	71	-	-	2	-	-	-	

^aAt end of test period

^btetraethyl lead

^cCooperative Fuel Research

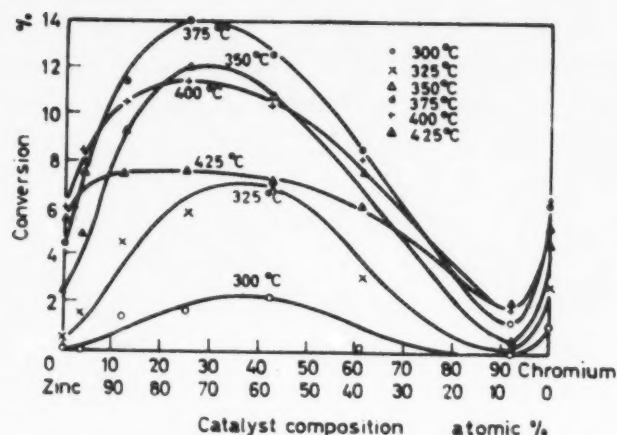


Figure 4-1. Conversion of CO to Methanol (Ref. 4-2).

4.2.3.3 Nonmetallic Catalysts

Nonmetallic catalyst materials are applied in petroleum cracking and reforming processes. These materials comprise the oxides of the Group 1 elements (periodic tables), and include alumina, magnesia, silica, and zirconia. Frequently, mixtures of these acidic oxides are utilized. In some applications such as the manufacture of aromatics by means of dehydrogenation and isomerization of paraffins, bifunctional catalysts are used, which consist of a metal and an acidic oxide. The function of the metal is to catalyze the hydrogenation-dehydrogenation reactions, while the oxide enhances the formation of the aromatics. These catalysts are fabricated by impregnating γ -alumina granules with a solution of chloroplatinic acid or by mechanically mixing the platinum and the oxide.

4.2.4 Substrates

Metallic catalysts are generally deposited on a suitable substrate material which acts as catalyst support. The substrate materials are selected to meet a number of requirements, including high-temperature capability, high porosity, low density, and high mechanical strength. Several candidate materials,

their maximum safe operating temperature, and the probable failure mode are listed in Table 4-6. The substrates are manufactured from these materials and can be either pellets, monolithic structures, or fibrous materials. In some special applications, metal wires or screens are used which are coated with the catalyst material.

4.2.4.1 Pellet Substrates

Aluminum oxide appears to be the material most frequently used in the manufacture of pellet type catalyst supports. These pellets, which can be of a variety of shapes ranging from small spheres to elongated cylinders, are manufactured by means of extrusion or drop tower processes. Spherical pellets are frequently preferred because of their lower attrition rate. Some heat treatment is required before the extrusion process to remove excess moisture. Depending upon the selected temperature-versus-time profile during dehydration of the pellets, α - or γ -alumina is obtained. Below 1750°F, the γ -phase of Al_2O_3 predominates. This material has a very high surface area, compared with the α -phase, which is formed at temperatures above 1750°F. Substrate surface area is a very important parameter because the activity of a catalyst is dependent upon the available surface area.

Table 4-6. High Temperature Porous Materials

Material	Safe Operating Temperature, °F	Probable Failure Mode
Al_2O_3 - SiO_2 fiber	1900	Sintering and crystallization
Si_2O_2 fiber	2000	Sintering and crystallization
SiC	2700	Oxidation
3 Al_2O_3 -2 SiO_2	2700	Sintering
Al_2O_3 (alpha)	3000	Sintering
ZrO_2	3200	Sintering

Pellet substrates are used primarily for chemical and petrochemical applications. Some automobile manufactures are considering pellet catalysts for use in emission control systems.

4.2.4.2 Monolithic Substrates

The monolithic type of substrate refers to a single unit structure, generally of honeycomb design to provide the necessary surface area. While referred to as monolithic, the structure may in fact consist of many layers of corrugated sheets stacked together to comprise the total unit. Currently, monolithic substrates coated with platinum group metal catalyst formulations are favored for industrial tail gas purification systems and catalytic converters for forklift truck applications. Also, monolithic platinum group metal catalysts have been selected by most automobile manufacturers for use in their 1975 model year automobiles (Ref. 4-7).

Two ceramic corrugated monolithic configurations, α -alumina (Al Si Mag [®] 614 and 775) and cordierite (Al Si Mag [®] 795) are being produced by American Lava. Al Si Mag is the trade name for alumina-silica-magnesia compounds. Cordierite is the mineralogical name of ternary oxide ($2 \text{MgO} \cdot 2 \text{Al}_2\text{O}_3 \cdot 5 \text{SiO}_2$) and this compound is the primary constituent in Al Si Mag [®] 795. As indicated in Table 4-7, the two types differ primarily in the porosity level. Al Si Mag [®] 614 has a higher temperature capability but shows lower thermal shock resistance (Ref. 4-9). Both rolled and stacked configurations are available (Figure 4-2). Currently, the stacked structures are preferred for automotive applications because of their superior durability under the very severe thermal conditions occurring in automotive installations.

Corning manufactures a truly monolithic, multi-cellular ceramic substrate by means of a proprietary extrusion-type process. This substrate configuration, which is designated W-1, has a square cell matrix and can be manufactured in a wide variety of shapes and sizes, as shown in Figure 4-3. Physical properties of the W-1 material are listed in Table 4-8 (Ref. 4-10).

Torvex ceramic honeycomb material is commercially available from DuPont in two compositions, alumina and mullite (Ref. 4-11). The alumina composition contains about 96 percent α -alumina, 3 percent magnesium aluminate, and 1 percent mullite ($3 \text{Al}_2\text{O}_3 \cdot 2 \text{SiO}_2$). The mullite formulation is composed of 55 percent mullite, 30 percent silica, and 15 percent α -alumina.

Table 4-7. American Lava Monolithic Substrate Physical Properties

Materials		Alsimag 614	Alsimag 776	Alsimag 795
		Dense 96% Alumina	Porous 96% Alumina	Cordierite
Property	Unit	Highest mechanical strength. Good corrosion resistance	For catalyst carriers and special applications	Good thermal shock resistance. Excellent as catalyst carrier
Water absorption	%	0	17	25-30
Safe operating temperature	°C °F	1,538 2,800	1,200 2,192	1,200 2,192
Specific gravity of material web		3.65	2.5	1.7
Specific heat	Btu/lb °F	0.21	0.21	0.19
Coefficient of thermal expansion	in/in/°F 70-1400°F	4.4×10^{-6}	3.9×10^{-6}	2.1×10^{-6}
Thermal shock resistance		Fair	Good	Excellent
Compressive strength (parallel to passages)	psi (5c/in SC) 0.016 thick web	15,500	8,500	2,750
Modulus of rupture	psi (4 in. centers, 1 x 1 in. beam, 5c/in SC)	2,800	1,500	1,800
Thermal conductivity	Solid ceramic at 570°F Btu in/hr-ft ² °F	119.0	85.0	10

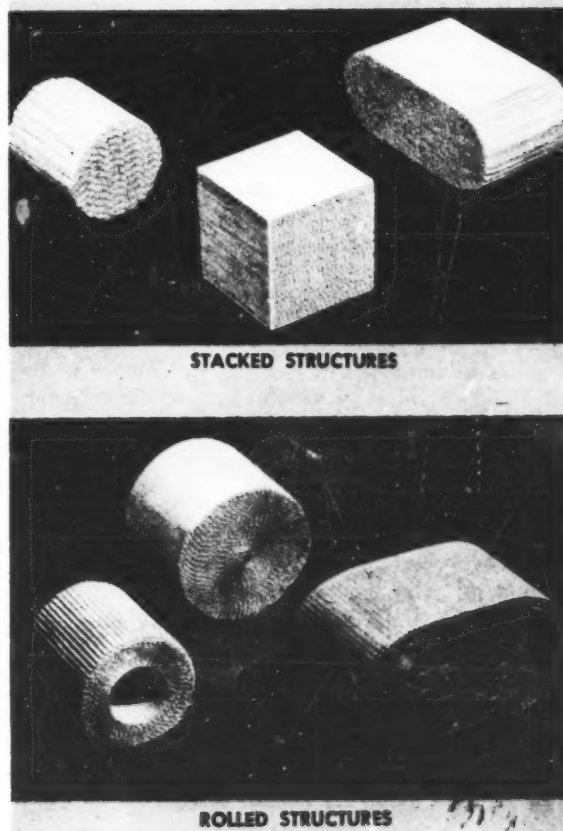


Figure 4-2. American Lava Stacked and Rolled Corrugated Structures

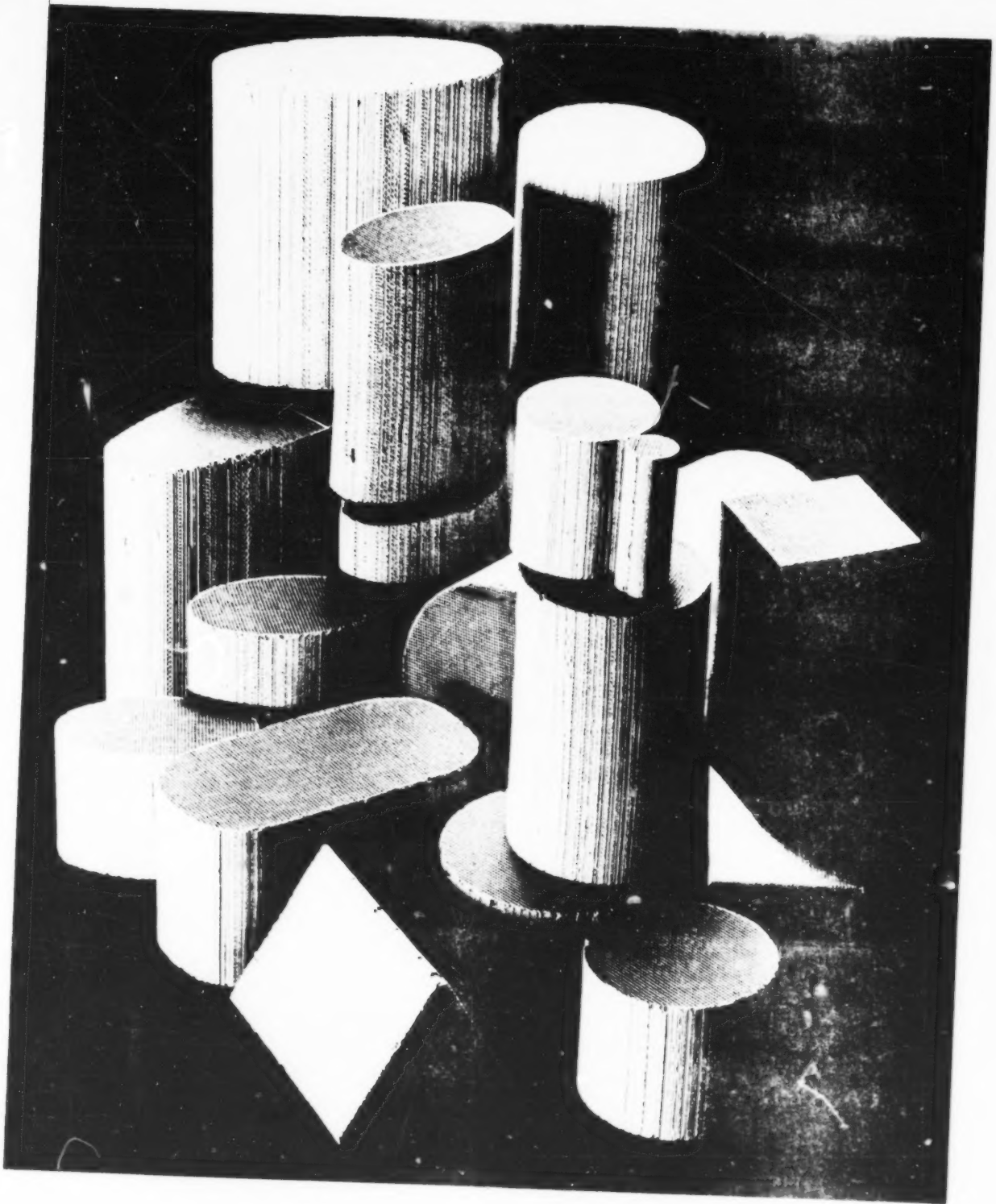


Figure 4-3. Corning Substrate Geometries

Table 4-8. Corning W-1 Monolithic Substrate
Physical Properties

MECHANICAL STRENGTH

Crushing resistance	
Axial	5,000 psi
Radial	500 psi
45°	50 psi
Impact, cumulative ft-lb 5 ft drop ^a	
Radial, 140 ft-lb	8% wt loss
Axial, 140 ft-lb	3% wt loss
Vibration, 280 cpm, amp 1.062 in, 80 min	11% wt loss
Thermal expansion, 75°F to 1830°F	1.25×10^{-6} in/in°F

STRUCTURAL UNIFORMITY

Bulk density	28 ± 2 lb/ft ³
Cell uniformity (0.06 × 0.06 in)	0.060 to 0.061 in
Wall uniformity (0.010-in thick wall)	0.010 to 0.0095 in
Cells/in ² (0.06 × 0.06 in cell, 0.01-in wall)	203 ± 5
Outside diameter (Nominal 4-5/8 in)	$\pm 1/32$ in
Open frontal area	74% $\pm$ 2%
Porosity, by mercury porosimeter	34%
Median pore size, by mercury porosimeter	7.5 microns

^a Mounted in converter assembly

The important physical properties of these materials are listed in Table 4-9. Three geometrically different configurations are being manufactured by DuPont for use as catalyst supports in tail gas abatement systems. These include a simple honeycomb structure, a slanted honeycomb design, and a crossflow-type structure that enhances flow turbulence and mixing.

According to DuPont the Torvex materials have a number of desirable features, including good thermal shock resistance, chemical inertness, high porosity, low bulk density, and high temperature capability. The alumina type has a safe operating temperature limit of about 2730°F and mullite is applicable up to 2460°F. In many cases, a wash coat is applied to the monolith before deposition of the catalyst material. The wash coat consists primarily of high porosity γ -alumina, which is added to increase the effective surface area of the substrate material for the purpose of maximizing catalyst activity. However, since γ -alumina is converted back to α -alumina at about 1750°F, the operating temperature must remain below that value to conserve the original effectiveness of the catalyst.

4.2.4.3 Fibrous Substrates

Fibrous substrate materials are manufactured from glass-ceramics or asbestos. This type of substrate is utilized primarily in low-temperature catalytic combustors manufactured by a number of companies for use in domestic, agricultural, and industrial heaters.

4.3 CATALYST DEGRADATION

Catalytic converter-combustor configurations pose fundamental durability problems related to the active catalyst constituents and the substrate materials. The service life of the catalyst is determined by two separate but interrelated aspects: performance durability and physical durability. The performance durability is most strongly impacted by decremental changes in catalytic activity caused by:

1. Contamination of the catalyst surface by poisonous compounds contained in the fuel and engine lubricating oil (e.g., lead, phosphorus, sulfur)

Table 4-9. DuPont Torvex Monolithic Substrate Physical Properties

	Ceramic Type	
	Alumina	Mullite
Composition	96 α -Al ₂ O ₃ /3 MgAl ₂ O ₄ / 1(3 Al ₂ O ₃ · 2 SiO ₂)	55(3 Al ₂ O ₃ · 2 SiO ₂)/ 30 SiO ₂ /15 α -Al ₂ O ₃
Maximum operating temperature, °F	2732	2462
Surface area, ft ² /ft ³	60 - 384	60 - 384
Cell size, in.	1/8 - 3/4	1/8 - 3/4
Bulk density, lb/ft ³	10 - 34	20 - 35
Porosity, percent	60 - 80	60 - 80
Wall thickness, in.	0.03 - 0.05	0.03 - 0.05
Thermal conductivity, $\frac{\text{Btu-in}}{\text{hr-ft}^2 \cdot ^\circ\text{F}}$	6 (at 1470°F)	6 (at 1470°F)
Coefficient of thermal expansion, cm/cm °C	0.5 x 10 ⁻⁵	0.5 x 10 ⁻⁵

2. Reduction in the porosity of the substrate surface as a result of alumina phase change occurring at excessive temperature
3. Alumina thermal shrinkage due to excessive temperatures

The physical durability of the catalytic unit is most strongly impacted by:

1. Thermal expansion differences between monolithic ceramic substrates and their supporting container
2. Local melting of monolithic ceramic substrates due to local overtemperature conditions
3. Failure of pellet retaining screens due to overtemperature
4. Cracking of monolithic ceramic substrates and breakup of pellet substrates due to vibratory loads

These factors are analyzed in the following sections.

4.3.1 Catalyst Poisoning

There is universal agreement that the effectiveness of a catalyst is reduced substantially when exposed to certain metallic and nonmetallic substances, such as lead, sulfur, and phosphorus. Among the possible poisoning mechanisms are the following:

1. Chemisorption of the poisonous materials on active surface sites, thereby impeding the reactions between the reactants and the catalyst
2. Deposition of a poison or coating on the catalyst surface, rendering the surface inaccessible to the reactants

Chemisorptive poisons are substances that are capable of forming stronger bonds with the catalyst surface than the bonds normally formed by reactants and products. According to Maxted (Ref. 4-12) the most toxic substances for metal catalysts are the elements of groups Vb and VIb of the Periodic Table of Elements, certain compounds containing metal ions, and molecules and ions with multiple bonds such as carbon monoxide.

Lead, sulfur, and phosphorus have been identified as particularly severe poisons for most metal catalysts. There are indications that base metal catalysts are less susceptible to poisoning by these elements than platinum group metal catalysts (Ref. 4-13). According to Wheeler (Ref. 4-14), catalyst

poisoning occurs either nonselectively or selectively. In the nonselective mode, the active surface of the catalyst is reduced uniformly by slow adsorption of the poison, which results in a gradual reduction in the catalyst efficiency. However, if the toxic substance is rapidly adsorbed, the mouths of the catalyst pores are then selectively poisoned. This results in a very rapid decline of the catalyst performance because the internal pore surfaces are then no longer available to participate in the chemical reactions.

4.3.1.1 Lead Effects

The effect of lead contaminant level in the fuel on the performance of an Engelhard PTX 3 automotive oxidation catalyst is illustrated in Figure 4-4 (Ref. 4-15). As indicated, the conversion efficiency decreases substantially with increasing lead content in the fuel. Since these data are based on constant speed operation of a spark ignition reciprocating engine, the data may not be directly applicable to catalytic combustors of the type projected for use in gas turbines. Also, the operating temperature of a catalytic combustor for gas turbines would generally be higher than the average temperature of an automotive catalyst, and this might alleviate potential lead poisoning problems to some degree. In any case, a detailed test program would be required to fully assess the effects of lead contaminant level in the fuel on the performance of catalytic combustors.

4.3.1.2 Phosphorus and Sulfur Effects

Very little information is available regarding the deleterious effects of sulfur and phosphorus on catalyst activity. Tests conducted by General Motors on automotive catalysts indicate no "significant" differences in the effects of these contaminants on base metal catalysts as opposed to noble metal catalysts (Ref. 4-16). According to General Motors, the sulfur problem could be alleviated if the catalyst temperature would be maintained above 1300°F at all times. Since most catalytic gas turbine combustors would be operated at temperatures above that level, except perhaps at idle, sulfur may not pose a serious problem in these applications. In General Motors' opinion, phosphorus is bad, regardless of the operating temperature.

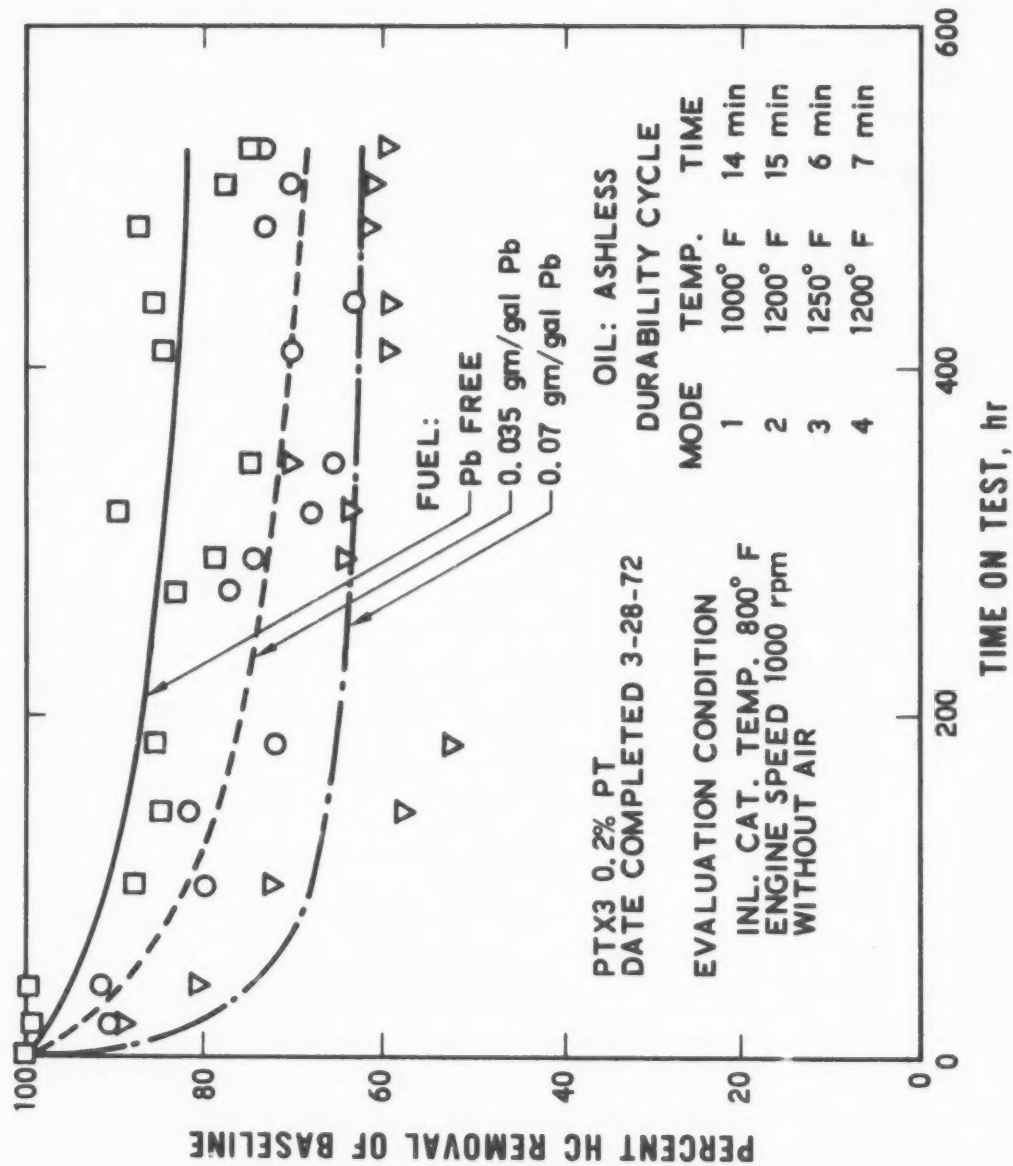


Figure 4-4. Effect of Lead Additive on Catalyst Efficiency (Ref. 3-15)

4. 3. 1. 3 Other Contaminants

Other potentially toxic substances contained in liquid fuels and lubricating oil include zinc, barium, halides and other trace elements.

Coking of catalyst surfaces has been observed in tail gas abatement systems under fuel-rich operating conditions. Although the effectiveness of the catalyst is reduced by the coking layer, the original effectiveness can be restored by operating the catalyst with excess air for some time.

Obviously, zero fuel and oil contaminant levels would be desirable, but practical considerations such as lead contamination of the fuel during shipment and the sulfur and trace metals normally found in kerosene-type fuels dictate that trace levels of these contaminants will have to be tolerated by catalytic combustors. The exact contribution of lubricating oil constituents to catalyst deactivation is not evident.

4. 3. 2 Alumina Phase Change

Pellet substrates used in automotive catalysts are generally composed of activated alumina material. Frequently, the monolithic substrates have a wash coat of γ -alumina which provides the high porosity required for high catalyst activity. Although the alumina material does not melt until a temperature of 3600°F is reached, it does undergo a phase change from γ -alumina to the low porosity α -alumina at 1750°F , which results in a substantial reduction in catalyst effectiveness.

4. 3. 3 Thermal Shrinkage

Pellet substrates are also subject to shrinkage in physical volume at elevated temperatures. The effect of the thermal shrinkage is to reduce catalyst effectiveness via reduced surface area and to cause "loosening" of the pellets in the catalyst container unless special design features are added to compensate for any loss in volume.

According to General Motors (Ref. 4-17), excessive shrinkage has occurred in early pellet designs at temperatures of about 1400°F. However, current pellets have satisfactory shrinkage properties up to 1800°F, and further improvements are likely.

No thermal shrinkage problems have been observed on monolithic substrates.

4.3.4 Thermal Differential Expansion

Both pellet and monolithic substrates have thermal expansion coefficients different from the catalyst canisters housing them. Upon bed warmup, the pellets can become looser in the bed than originally packed. Monolithic catalyst elements also can become "loosened" with respect to the container. Both may then be subject to mechanical attrition effects, as discussed in Section 4.3.6.

4.3.5 Melting

The cordierite material used for monolithic substrates has a melting point of approximately 2500°F to 2600°F. Even though the overall bed temperature might be below this level, it is conceivable that local zones of the catalyst might be subjected to overtemperature unless a homogeneous fuel-air mixture is provided.

4.3.6 Vibration Effects

Although vibration levels in gas turbines are generally very low, it is considered appropriate to dwell briefly upon the deleterious effects that excessive vibratory loads can have on the durability of catalysts. In automotive installations, breakup of pellet and monolithic catalysts has been observed by a number of small-car manufacturers (Ref. 4-7). Apparently, this problem is related to high second order vibrational loads occurring in 4-cylinder engines. Although this problem has not yet been resolved, it appears that catalyst/substrate attrition and cracking could be alleviated by utilizing properly designed containers.

4.4

CATALYTIC CONVERTERS AND COMBUSTORS

Very little work has been conducted to date by industry and governmental agencies on high-temperature catalytic combustors of the type applicable to gas turbines and stationary power plants. The only known data in this particular area were taken by Engelhard (Ref. 4-18) and by the Control Systems Laboratory of EPA (Ref. 4-19). In both cases, small catalytic combustor sections were tested over a limited range of operating conditions.

To provide the information required for a meaningful assessment of high-temperature catalytic combustors, it is considered appropriate to briefly discuss the operational characteristics and the problem areas related to the following catalytic converter/combustor categories:

1. Automotive oxidation catalysts
2. Tail gas abatement systems
3. Low-temperature catalytic burners
4. High-temperature catalytic burners

4.4.1

Automotive Oxidation Catalysts

Oxidation catalysts are being considered by all domestic automobile manufacturers as principal emission control system components projected for their 1975 and later model year cars. The catalytic converter type that appears most frequently in the first-choice systems is the platinum group metal-monolithic configuration, exemplified by the Engelhard PTX design. These catalysts are installed downstream of the engine exhaust manifold in order to convert the unburned hydrocarbon and carbon monoxide species leaving the engine. Under normal operating conditions of the engine, the catalyst temperature is of the order of 1200°F to 1400°F. However, at high engine loads, the temperature increases to about 1700°F to 1800°F, and even higher temperatures have been observed at excessively fuel-rich operating conditions of the engine. The monolithic catalysts are designed for space velocities of the order of 100,000 hr⁻¹.

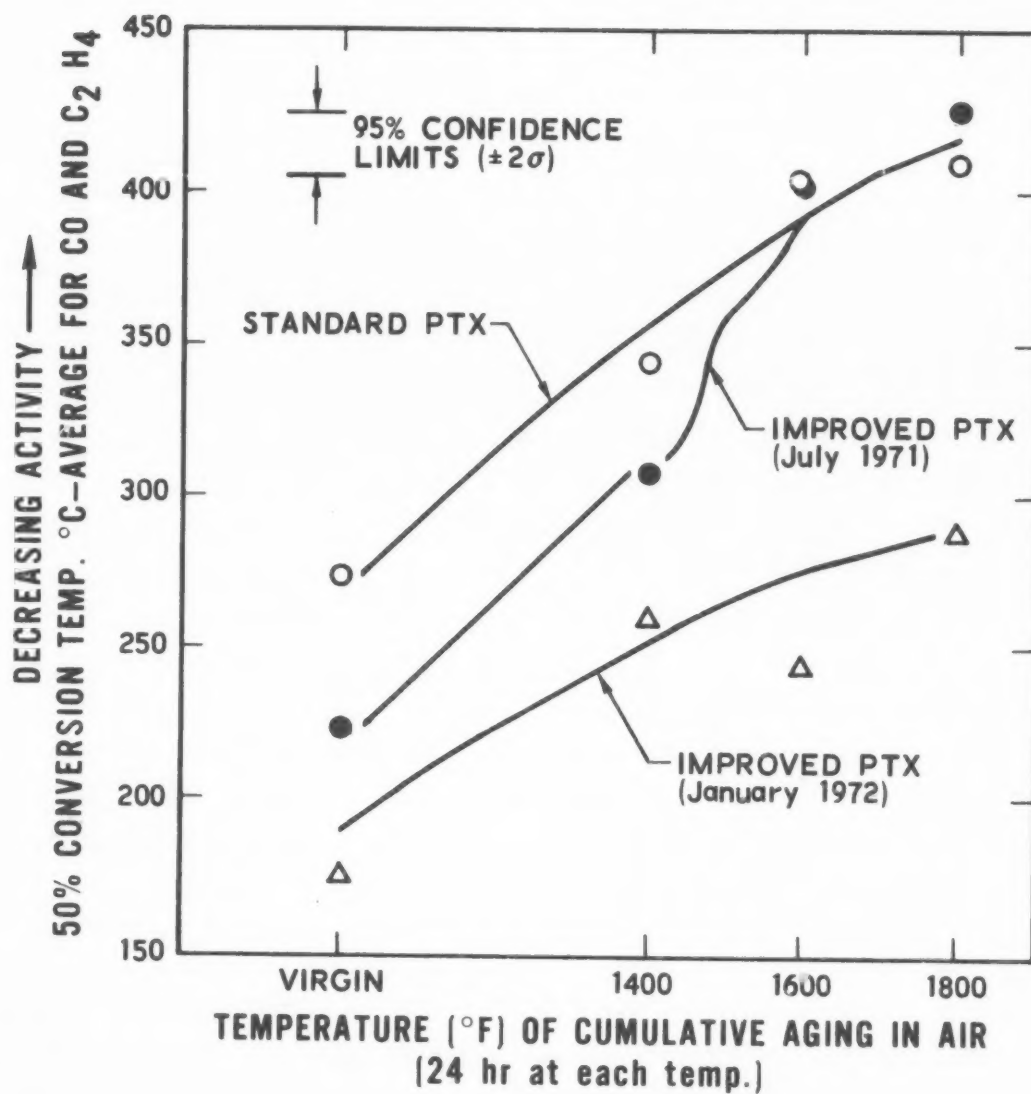


Figure 4-5. Engelhard Monolithic Catalysts with Improved Catalytic Thermal Stability (Ref. 4-20)

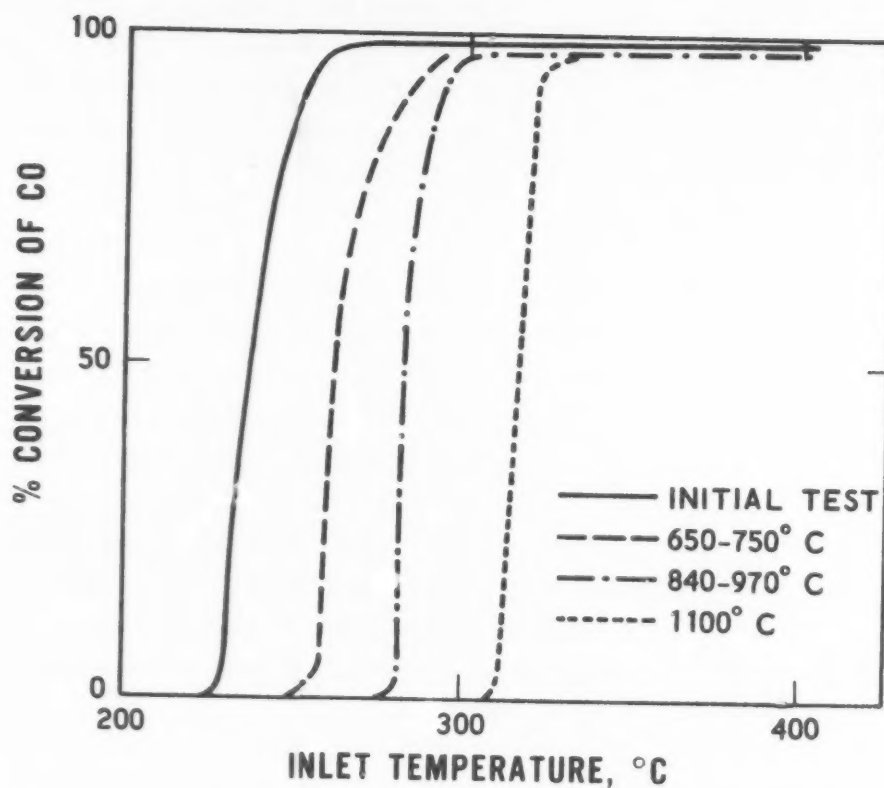
The most pervasive problem relative to the 1975 emission control systems appears to be the lack of adequate catalyst durability. When fresh, the performance of many catalysts is adequate to meet the Federal emission standards for light-duty vehicles. However, with increasing car mileage, the effectiveness of the catalyst deteriorates steadily due to the combined effects of poisoning by lead, sulfur, and phosphorus contained in trace quantities in the fuel, and to catalyst overheating which can occur under extreme engine operating conditions. Catalyst failures have occurred also as a result of cracking and local melting of the substrate material, attributed to excessive vibratory loads and overtemperature conditions.

The catalyst durability problem is treated in several ways. One of these is the use of improved substrate materials. Another technique involves improvements in the control of the catalyst operating environment. In addition, efforts are under way to improve the lightoff and thermal stability characteristics of the catalysts. The progress made by Engelhard in this regard is illustrated in Figure 4-5 (Ref. 4-20). These data show the greatly increased retention of activity of the improved catalyst, even after severe thermal aging. Similar results were reported by Matthey Bishop (Ref. 4-21). As shown in Figure 4-6, the lightoff temperature of the Matthey Bishop improved catalyst increases with aging temperature. However, the steady-state efficiency of the catalyst is essentially unaffected by aging.

There are some indications that certain base metal catalysts might have lower lightoff temperatures than noble metal catalysts. This is illustrated in Figure 4-7 which presents HC and CO conversion efficiencies determined by General Motors in bench tests of noble metal and base metal catalysts (Ref. 4-17).

4.4.2 Tail Gas Abatement Systems

Catalytic units are employed in a number of tail gas abatement systems used by the chemical process industry to reduce the hydrocarbon and nitric oxide



**STATIC ENGINE DURABILITY TEST:
EFFECT OF TEMPERATURE OVER
A 24-hr TEST ON AEC 3A**

Figure 4-6. Effects of Thermal Aging on Matthey Bishop AEC3A Catalyst (Ref. 4-21)

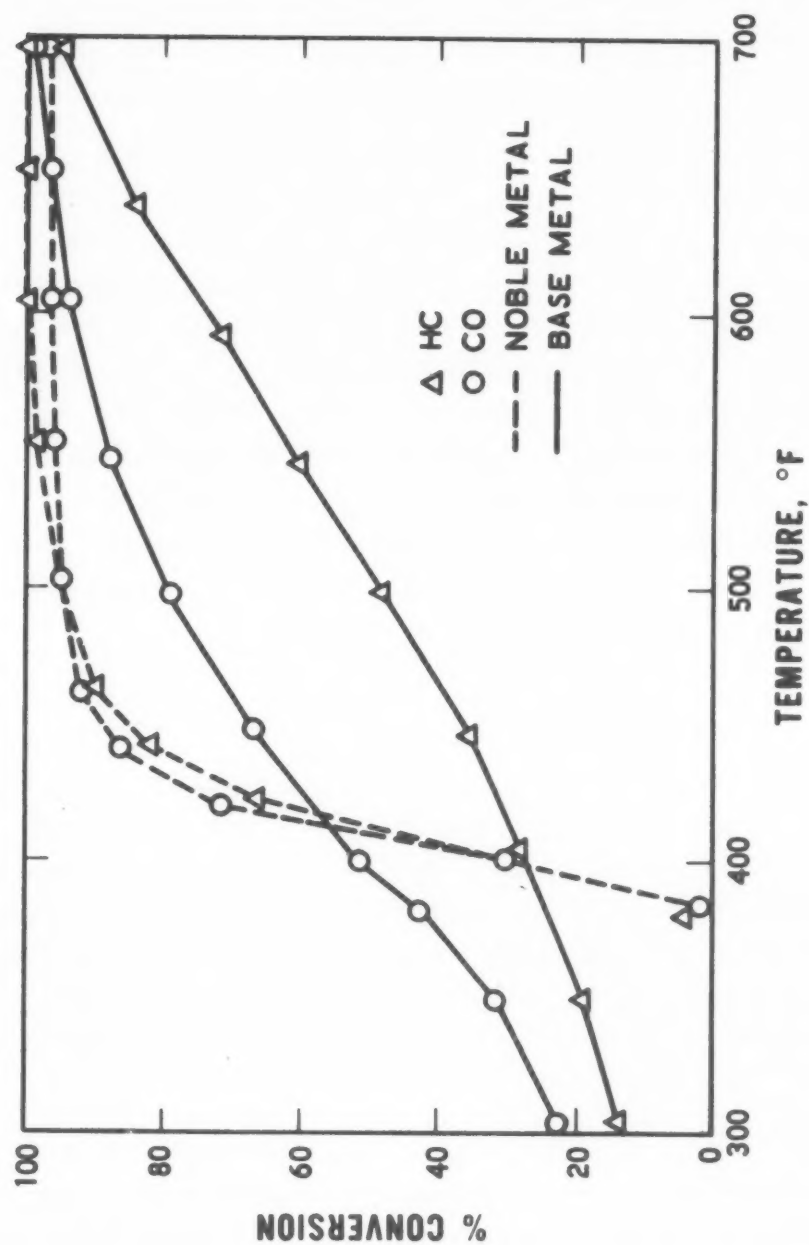


Figure 4-7. Conversion Characteristics of Base Metal and Noble Metal Catalysts (General Motors Bench Test Evaluation) (Ref. 4-17)

emissions from these processes. The operational characteristics of these systems are briefly discussed in the following sections.

4.4.2.1 Hydrocarbon Fume Abatement

In the past, direct flame incineration was the favored hydrocarbon fume abatement method. More recently, catalytic combustion has become attractive, primarily for economic reasons. According to a study conducted by Hein (Ref. 4-22), the cost of fume abatement by the lower temperature catalytic process is only about 20 to 70 percent of the cost of direct flame burners, depending upon the particular application. Based on the encouraging results obtained by a number of investigators at UCLA (Refs. 4-23 to 4-25) in the area of catalytic oxidation of various hydrocarbon species, DuPont carried out an experimental program to establish the feasibility of catalytic combustors in fume abatement systems. In these tests, platinum catalysts were used in conjunction with pellet and Torvex mullite monolithic substrate configurations (Ref. 3-26 and 3-27).

With regard to catalyst manufacture, the pellet substrate materials were first coated with a γ -alumina wash coat, which has a specific active surface area of 180 to 200 m^2/gm . The monolithic substrates, which have a superficial surface area between 1.17 and 1.26 m^2/liter of substrate, were coated also with γ -alumina to provide a catalytic surface area of about $2.5 \times 10^4 \text{ m}^2/\text{liter}$. The platinum was deposited on the substrate from an aqueous solution by chemical reduction, or by solution impregnation and subsequent hydrogen reduction. The platinum loadings used were 2 and 3 percent of the γ -alumina mass. The catalysts were operated at space velocities between 30,000 hr^{-1} and 175,000 hr^{-1} .

The pressure drop characteristics of these catalytic combustor units are presented in Figure 4-8. As indicated, the straight cell honeycomb has the lowest pressure drop, followed by the cross-flow honeycomb and the spherical pellet configuration.

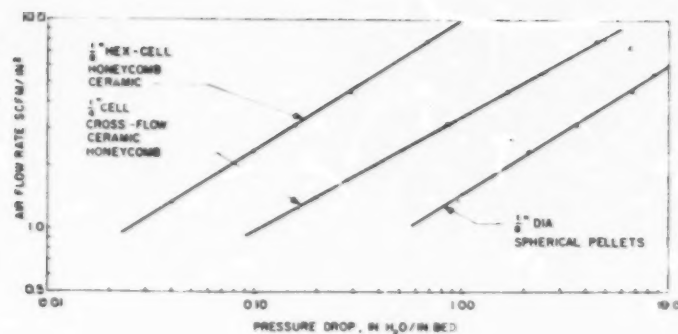


Figure 4-8. Pressure Drop of Monolithic and Pellet Catalysts (Ref. 4-26)

Fume abatement effectiveness data obtained by DuPont are shown in Figures 4-9 through 4-12 (Ref. 3-26). Figure 4-9 presents the conversion efficiency of n-heptane as a function of reactor inlet temperature for a cross-flow honeycomb catalyst, a spherical catalyst, and, for comparison, a direct-flame combustor. As indicated, the catalytic burners are substantially more effective at the lower temperatures. These characteristics clearly show the advantage of catalytic combustors, which can operate efficiently at rather low flow inlet temperatures. This results in substantial fuel cost savings.

The effects of space velocity on the lightoff temperature of the straight-flow honeycomb, cross-flow honeycomb, and spherical pellet catalysts are depicted in Figures 4-10 through 4-12. In each case, the lightoff temperature increases with increasing space velocity. The cross-flow honeycomb design has the lowest lightoff temperatures of the three configurations.

Based on these results, it is concluded that catalyst geometry and size have a strong effect on the performance characteristics of catalytic combustors, especially in the low temperature regime. DuPont feels that its honeycomb support offers excellent conversion efficiency at low pressure drop.

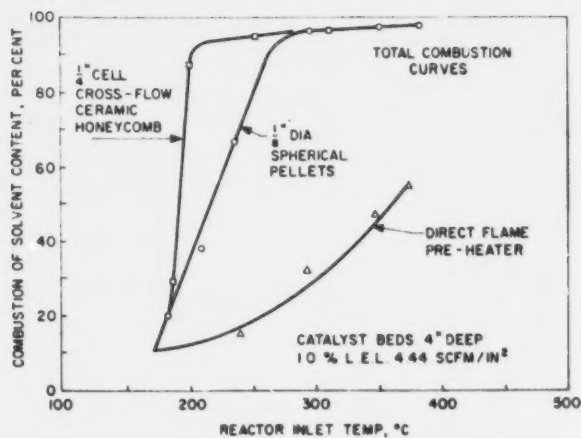


Figure 4-9. n-Heptane Fume Abatement Effectiveness (115,000/hr space velocity) (Ref. 4-26)

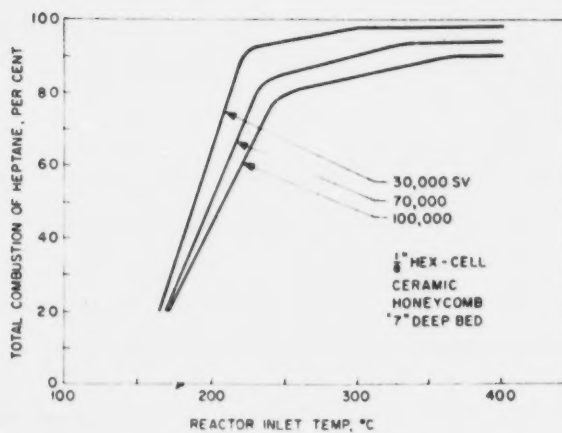


Figure 4-10. n-Heptane Conversion Efficiency vs Temperature and Space Velocity--Torvex Straight-Through Honeycomb (Ref. 4-26)

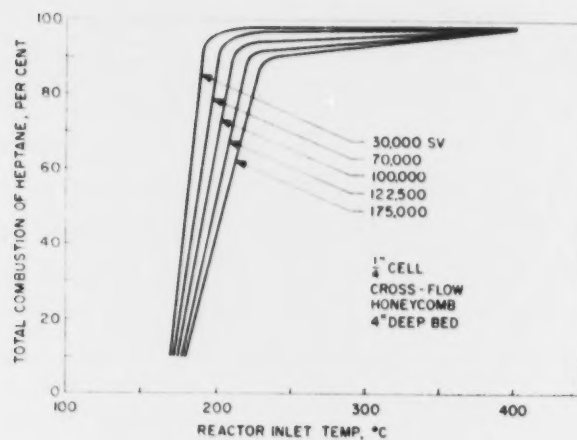


Figure 4-11. n-Heptane Conversion Efficiency vs Temperature and Space Velocity-- Torvex Cross-Flow Honeycomb (Ref. 4-26)

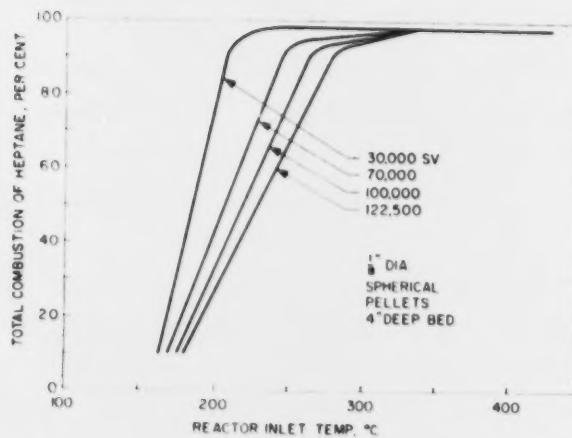


Figure 4-12. n-Heptane Conversion Efficiency vs Temperature and Space Velocity-- Granular Catalyst Substrate (Ref. 4-26)

The lightoff characteristics of a number of other hydrocarbon fuels oxidized in a monolithic platinum catalyst and a monolithic palladium catalyst are presented in Figures 4-13 and 4-14 (Ref. 4-27). In each case, the hydrocarbon concentration was 10 percent of the corresponding lower explosive limit (LEL) of the fuel. For methane, the LEL value in air is 5 percent, and for the other compounds the LEL in air varies between approximately 1 and 3 percent. Comparison between Figures 4-13 and 4-14 indicates that platinum is more active than palladium in catalyzing n-heptane. In these tests, methane has been the most difficult fuel to oxidize. Similar results were obtained by Accomazzo and Nobe (Ref. 4-24) with a copper oxide pellet catalyst. With increasing carbon number in the fuel, they observed a marked reduction in catalyst lightoff temperature.

The effects of platinum content, chemical composition of the substrate, and substrate surface area are illustrated in Figure 4-15. As shown, the catalyst lightoff characteristics are rather insensitive to variations in these parameters. It is conceivable, however, that catalyst aging effects might vary for the different catalyst loadings.

4.4.2.2 Nitric Oxide Tail Gas Abatement

Catalytic combustors are widely used in nitric oxide abatement systems employed in nitric acid manufacturing plants. In these plants, nitric oxide is generated via catalytic oxidation of ammonia over a platinum-rhodium catalyst. The nitric oxide then reacts with residual oxygen and forms nitrogen dioxide which is absorbed in water to form the nitric acid. The high pressure gases leaving the tower are composed of approximately 0.3 percent $\text{NO} + \text{NO}_2$, 3 percent O_2 , and 96 percent N_2 , and are expanded through a turbine to obtain useful power (Refs. 4-28 and 4-5). To maximize the power output of the turbine and to eliminate the NO , the tail gases are heated before expansion by catalytic combustion of the NO_2 . This is accomplished by injecting a reducing gas, such as methane or hydrogen, into the gas stream and oxidizing the mixture catalytically to form NO , CO_2 ,

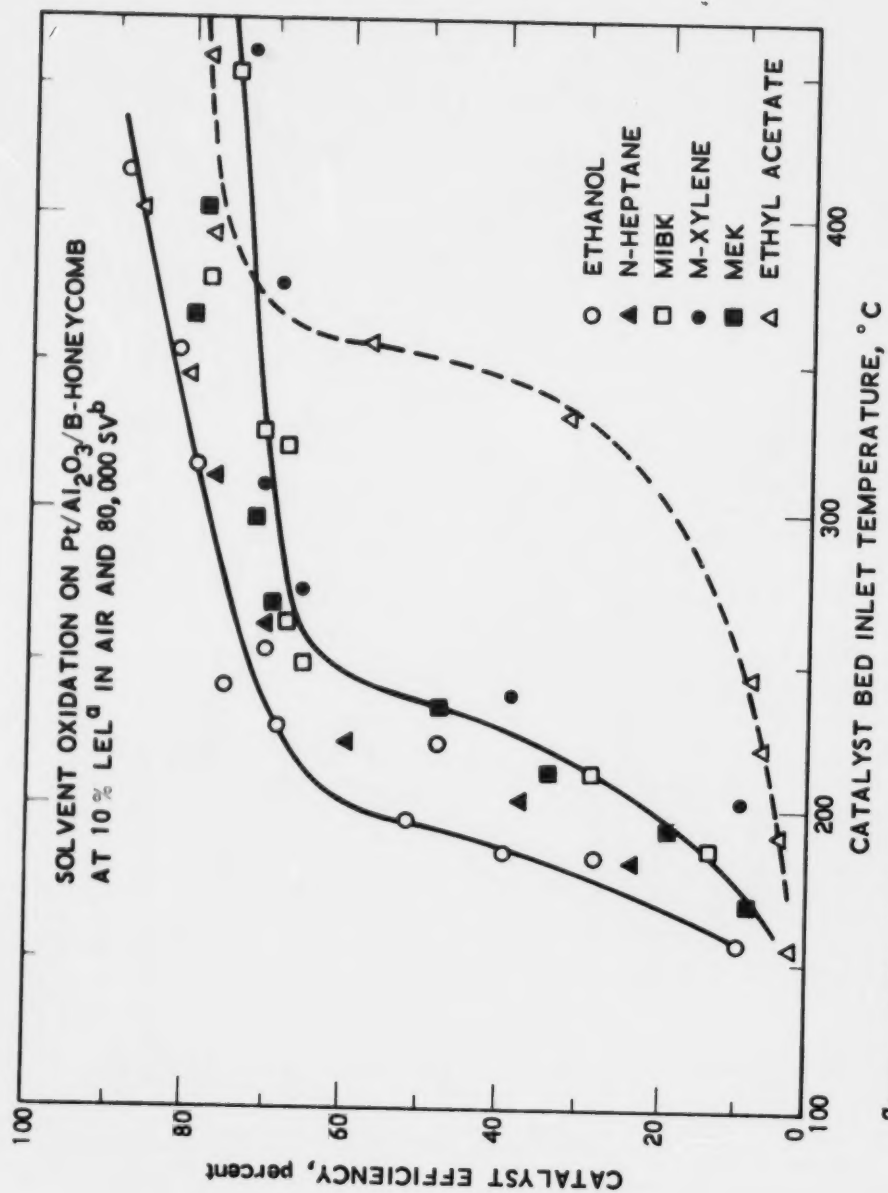


Figure 4-13. Lightoff Characteristics--Platinum Catalyst (Ref. 4-27)

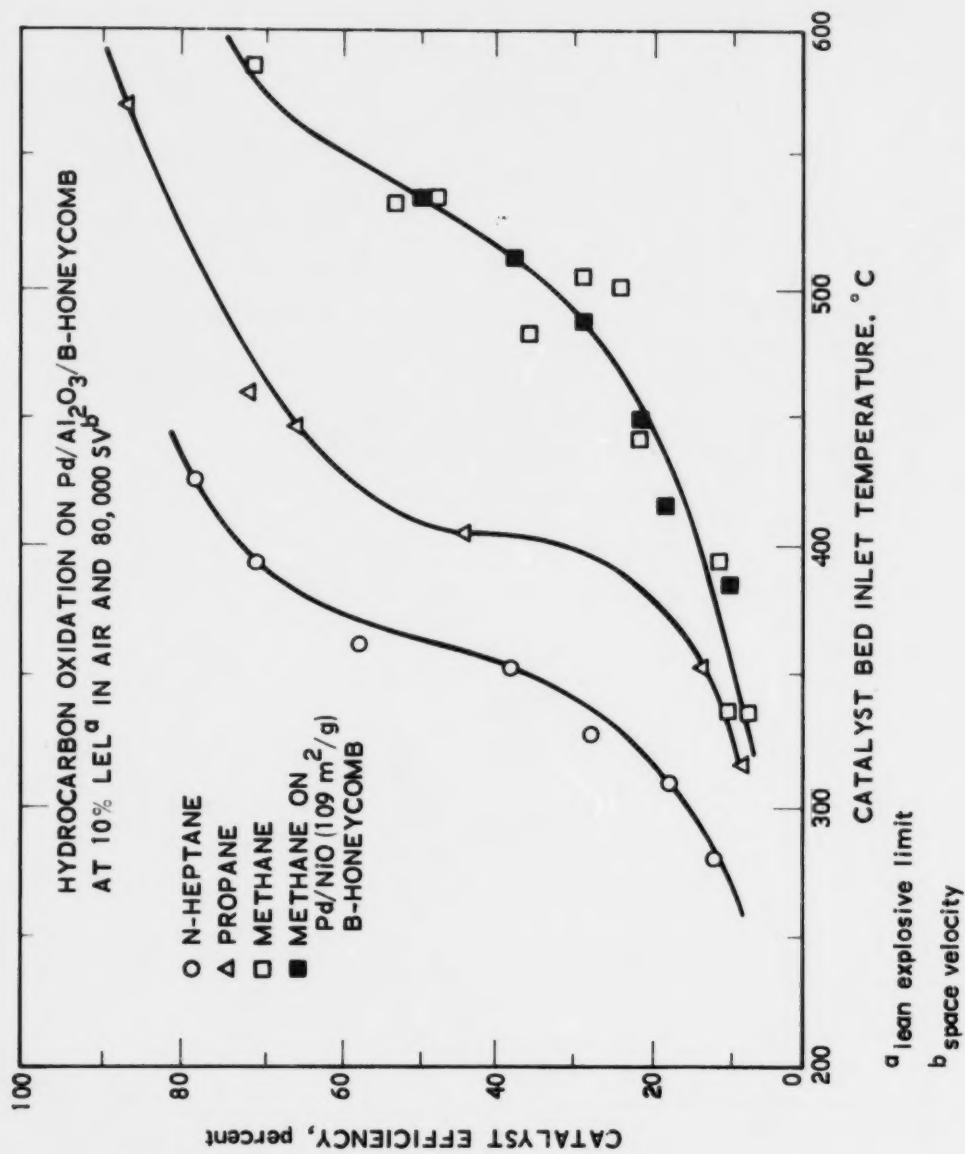


Figure 4-14. Lightoff Characteristics--Palladium Catalyst (Ref. 4-27)

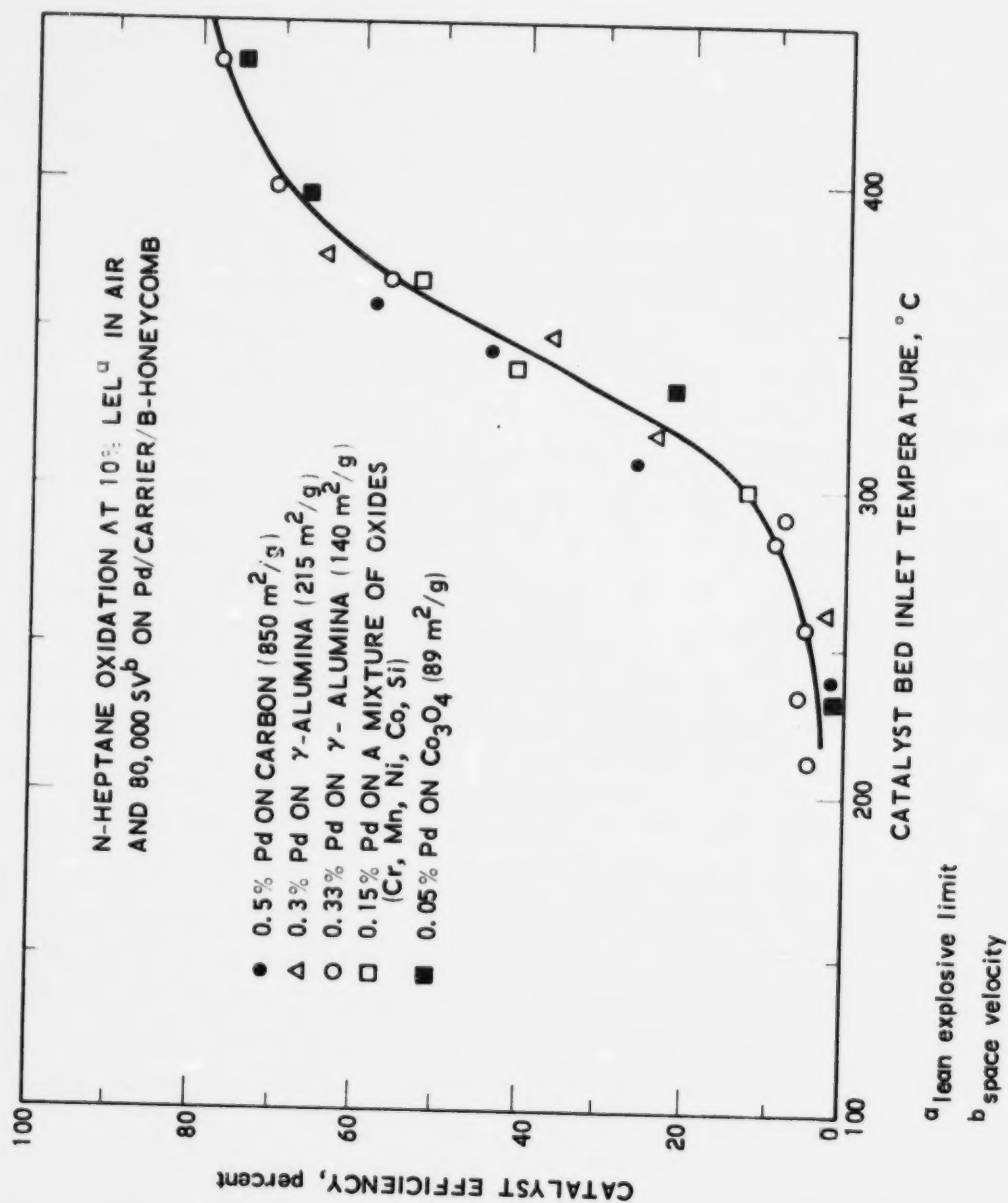


Figure 4-15. Palladium Catalyst Performance (Ref. 4-27)

and H_2O . This portion of the total abatement is the so-called decolorization phase because all the reddish-brown NO_2 is converted to invisible NO . By injecting additional fuel, all O_2 is oxidized and the NO is then converted to N_2 . Although theoretically, all NO is converted in the process, the efficiency of actual abatement systems is somewhat lower. Chemico feels that conversion efficiencies of about 90 percent are feasible on a long-term basis (Ref. 4-29).

In general, platinum and palladium catalysts, supported on pellet or monolithic honeycomb substrates, are utilized in NO abatement systems. Units of this type have been operated continuously for six to eight years (Ref. 4-28). Experience with these combustors has indicated that pellet catalysts are more durable, while the honeycomb configurations have size and pressure drop advantages. According to Engelhard, space velocities of the order of $100,000 \text{ hr}^{-1}$ are feasible for monolithic configurations, while pellet designs are limited to about $30,000 \text{ hr}^{-1}$. Natural gas, which contains a high percentage of methane, is the most popular fuel for use in NO abatement units. As illustrated in Figure 4-14, methane has a higher lightoff temperature than most hydrocarbons and this requires preheating of the tail gas to about 500°C in order to achieve acceptable conversion efficiency.

Typical catalyst operating temperatures are of the order of 1500°F , which represents the limit for continuous operation for both honeycomb and spherical substrate configurations considered by Engelhard for this application (Ref. 4-28). For short durations, the temperature can be safely increased to about 1650°F , without decreasing catalyst life. If synthetic gas containing hydrogen is available the catalyst inlet temperature can be reduced to about 400°F and, as a result, the exit temperature remains sufficiently low to assure long catalyst life (Ref. 4-28).

Initially, excessive performance degradation was observed on these catalysts as a result of a loss in active catalyst surface area; the loss was caused by sintering of the refractory substrate materials. Subsequently, stabilized substrates were developed in which the active surface area was increased

and sintering was minimized. As shown in Figure 4-16, the durability of the stabilized catalyst is excellent (Ref. 4-28).

The effect of space velocity on unaged and aged stabilized catalysts is shown in Figure 4-17. As indicated, the performance of the fresh catalyst is constant over the range of space velocities shown. Conversely, the effectiveness of the aged specimen decreases substantially as space velocity is increased above $100,000 \text{ hr}^{-1}$.

According to Engelhard (Ref. 4-5), catalyst performance and durability are strongly impacted by carbon deposition, catalyst poisoning, and overtemperature. All these factors result in lower catalyst effectiveness, higher lightoff temperatures, and reduced catalyst life. In general, carbon deposition is related to excess fuel and/or poor air-fuel mixing upstream of the catalyst. The deposits can be removed by carefully operating the catalyst in an oxidizing atmosphere for short periods of time.

Although the effects of poisonous ingredients in the tail gas have not yet been quantified, Engelhard feels that sulfur, halogens, and iron oxide are bad for its catalysts. Apparently, platinum catalysts are less affected by sulfur than are palladium catalysts. However, the higher activity of palladium usually justifies incorporation of a desulfurization step in the abatement process.

C & I Girdler, a manufacturer of nitric acid plants, has evaluated a number of catalytic combustor units designed for use in NO abatement systems (Ref. 4-30). Based on Girdler's own test data, it has selected pellet catalysts as first choice for use with methane. However, for economic reasons, monolithic platinum or palladium catalysts may be more attractive for those applications in which hydrogen-bearing purge gas is available.

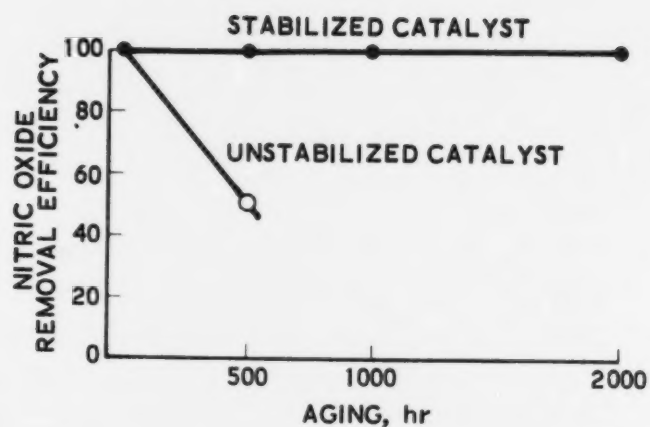


Figure 4-16. Performance of Stabilized and Nonstabilized Catalysts--Nitric Oxide Abatement (Ref. 4-28)

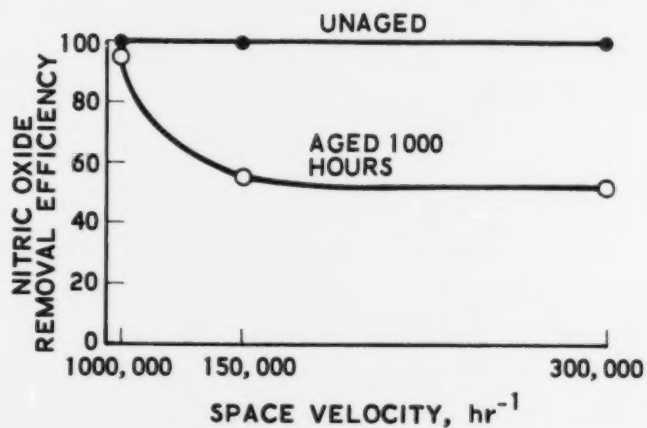


Figure 4-17. Performance of Stabilized Aged and Unaged Catalysts vs Space Velocity--Nitric Oxide Abatement (Ref. 4-28)

4.4.3

Low-Temperature Catalytic Combustors

For the purpose of this study, low-temperature catalytic combustors are characterized by operating temperatures below about 800°F. Although no visible flame is produced under these conditions, the amount of heat generated by the combustor is equal to the heat produced in a conventional flame-type burner. Typically, the specific heat release rate of a catalytic burner of this type is less than 100 Btu/hr-in². This type of burner is commercially available from a number of manufacturers for use in domestic, recreational, agricultural, and industrial heating and drying operations. Because of its low surface temperature, the burner offers a safety feature not available with conventional burners.

A typical low-temperature catalytic combustor unit is shown schematically in Figure 4-18 (Ref. 4-31). In this design, gaseous fuel enters through the metering orifice into the metal dish, which is designed to evenly distribute the gas to all parts of the burner. The active catalyst material is deposited on the front surface of the ceramic or asbestos fiber pad which serves both as catalyst support and as an insulator to minimize back radiation (Ref. 4-32).

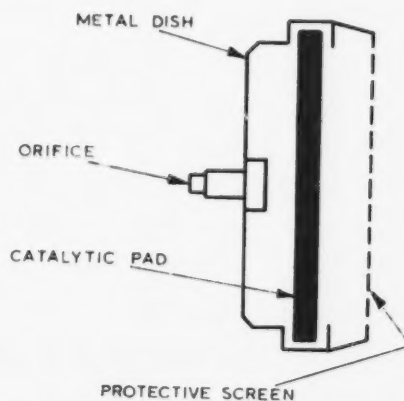


Figure 4-18. Catalytic Space Heater Schematic (Ref. 4-31)

In general, platinum is used as the catalytic agent, although less expensive base metals are sometimes added as promoters to enhance the catalyst oxidation reactions. As discussed in Section 4.4.1, base metal catalysts may have a lower lightoff temperature. Combustion takes place on the surface of the coated fibers, which are protected by a wire screen. The air required for combustion is drawn in through the wire screen. Generally, because of the associated improvement in air recirculation to the burner surface, the performance of these units improves with increasing ratio of perimeter to cross-sectional area of the pad. Burner lightoff is accomplished by preheating the catalyst bed either electrically or by means of a pilot light. The low-temperature combustor test data indicate very high HC emissions. In conventional combustors the HC emissions are generally much lower.

The AGA, Matthey Bishop, and the EPA have tested a number of different low-temperature catalytic combustors. The pertinent information provided by these organizations is briefly discussed in the following sections.

4.4.3.1 American Gas Association

Several years ago, the AGA conducted a research program aimed at the development of catalytic burners for use in kitchen ranges and other related applications. As part of that effort, a number of catalytic units were tested and evaluated. The substrate material used in these designs consisted of asbestos fiber pads which were procured from four different manufacturers. The substrates were coated in-house with a variety of catalyst materials, including platinum, palladium, platinum-palladium mixtures, and non-noble metals. The program was limited to gaseous fuels, primarily natural gas and liquified petroleum gas (LPG). Manufactured natural gas was utilized in some of the tests. The burner temperatures were held below approximately 900°F, which was the desired limit for the projected application. In the course of the program, a number of serious problems were encountered including incomplete combustion of the fuel and unpredictable burner lightoff characteristics. The program was canceled by AGA before completion (Ref. 4-33).

4.4.3.2

Control Systems Laboratory, EPA

In 1971, the Control Systems Laboratory of the EPA conducted an experimental program to assess the potential of catalytic combustion for pollution-free domestic heating applications (Ref. 4-34). A total of eleven commercially available catalytic heaters were tested. Eight of these units were operated with propane and three with lead-free gasoline.

The emission data obtained by the EPA are shown in Table 4-10. As indicated, the NO_x emissions are very low on all units. The CO emissions of the gas-fired heaters varied between 20 and 1560 ppm, while the liquid-fueled units had CO emissions between 665 and 2350 ppm. The HC emissions of the gas-fired units were significantly lower than those of the liquid-fuel designs. Apparently, there is no correlation between emissions and burner heat output. The specific heat release rates of the burner (Btu/hr-ft^2) are also presented in Table 4-10. Again, there is no correlation between the emissions and this particular parameter.

In an effort to resolve the large differences in the emissions obtained with these burners, the EPA conducted a series of parametric tests using the old Turner burner listed in Table 4-10 as the test unit. Variation of the thickness of the catalyst pad had some effect on the HC and CO emissions. Minimum HC and CO emissions were obtained with a one-inch pad. Doubling the platinum content in the pad resulted in some reduction in HC, but increased the CO emissions. However, this unexpected trend may well be the result of measuring inaccuracies.

By far, fuel flow rate has been the most important parameter with regard to HC emissions. This is because the combustion is controlled by the rate of oxygen diffusion to the pad surface. As illustrated in Figure 4-19, the HC emissions are minimum at a fuel flow rate of about $650 \text{ cm}^3/\text{min}$, standard. Over the range of fuel flow rates considered, the CO emissions are almost independent of fuel flow.

Table 4-10. Emissions from Commercial Catalytic Heaters at Maximum Heat Output^a

Heater Type	Rated Heating Value, Btu/hr	Measured Heating Value, Btu/hr	Specific Rated Heat Release Rate, Btu/hr-in ²	Concentration, ppm (air-free)		
				NO	CO	HC
<u>LPG MODELS</u>						
Bernzomatic	7000	4800	159	2	46	2,550
Cargo safe	6000	5970	52	16	124	8,650
Impala	8000	5970	79	8	174	4,050
McGinnis	8000	7785	35	6	20	1,000
Primus	8000	6365	N.A.	12	1,560	10,250
Turner (old style)	7000	3375	93	0	27	1,110
Turner (new style)	7000	4200	93	4	36	1,335
Zebco	7000	8040	93	0	205	370
<u>WHITE GAS MODELS</u>						
Coleman (old style)	8000	8440	N.A.	13	2,350	19,000
Coleman (new style)	5000	4750	N.A.	8	665	7,500
Thermos	7000	4915	N.A.	32	1,280	18,000

^aFuel control valves set on "High"

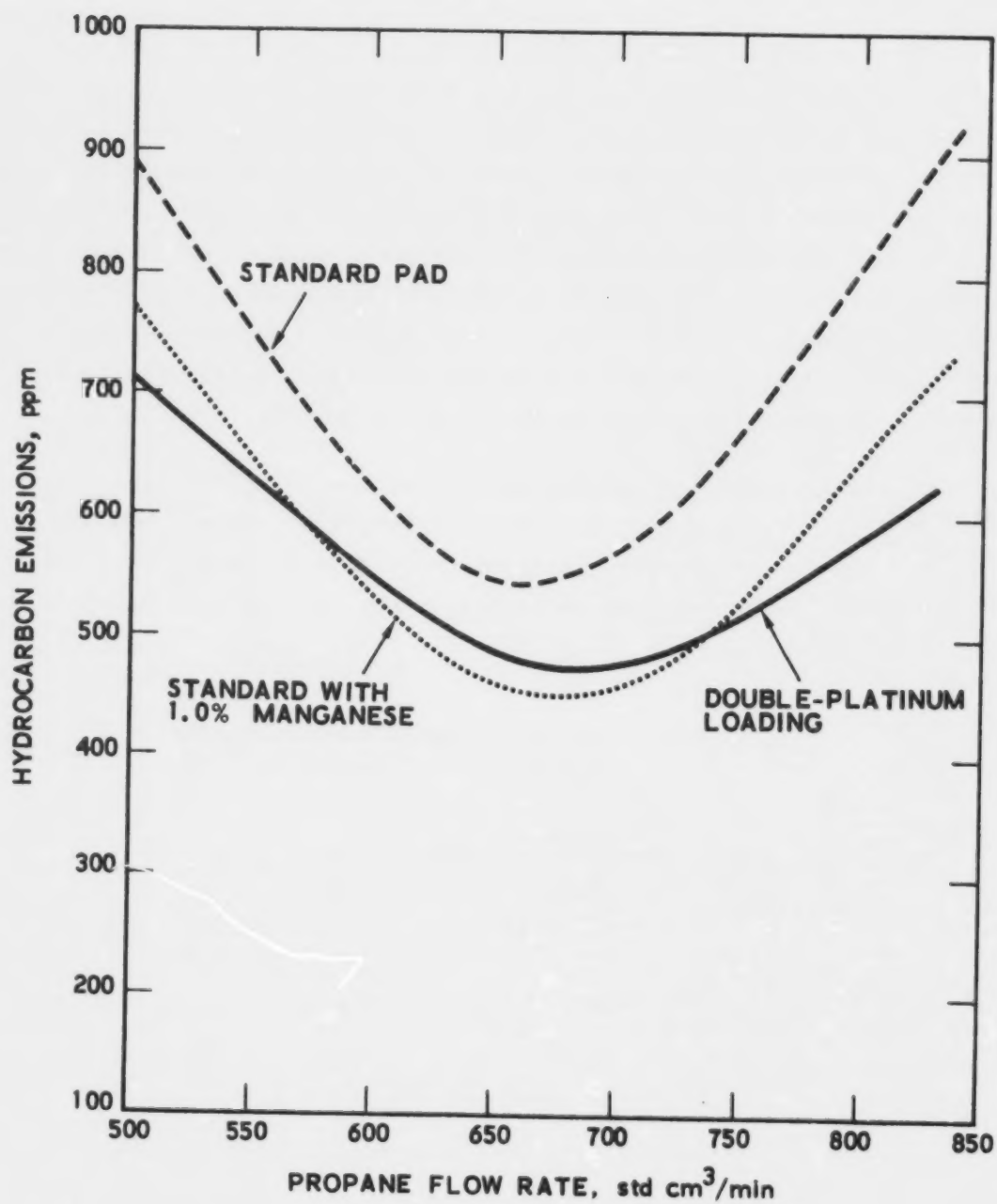


Figure 4-19. Hydrocarbon Emissions vs Fuel Flow Rate--
Catalytic Space Heater (Ref. 4-34)

4.4.3.3

Matthey Bishop, Inc.

Matthey Bishop has developed a number of platinum group catalysts for use in low temperature heater applications. These units, which are known as Cataheat systems, are designed to operate on various fuels including methane, propane, butane, natural gas, and white gasoline (Ref. 4-31). In the gaseous fuel designs, combustion is initiated by means of a pilot light or simply by lighting a match. In the liquid-fuel units, the fuel is brought up to the catalyst pad by means of a wick arrangement. According to Matthey Bishop, the life of the catalyst is strongly affected by impurities contained in the fuel. If pure hydrocarbons are used, the life should be infinite.

Emission data provided by Matthey Bishop are listed in Table 4-11 along with other pertinent information. As indicated, the CO emissions, adjusted to air-free operation of the burners, are between 100 and 150 ppm. However, the HC emissions are rather high, running between 1500 and 6000 ppm of hexane for the three burners.

Table 4-11. Matthey Bishop Catalytic Heater Characteristics (Cataheat System)

Type	Rating J/m^2 Btu/in^2	Air-free CO Measured by AGA Procedures, ppm	Approx. Ignition Temp., $^{\circ}\text{C}$	Approx. Surface Temp., $^{\circ}\text{C}$	Unburned Hydrocarbons as Hexane, ppm	Life, h
Cataheat L (liquid)	123×10^6 (75)	125	250-280	300-420	6000	5000+
Cataheat P (HD5 propane)	123×10^6 (75)	100	250	290-500	1500	10,000+
Cataheat M (methane- West Texas natural gas)	123×10^6 (75)	150	330	360-470	5000	10,000+

4.4.4 High-Temperature Catalytic Combustors

Because of their low NO_x emissions potential, catalytic combustors are now being considered by a number of organizations for use in automotive, aircraft, and stationary gas turbines. The majority of the mobile engines are designed for turbine inlet temperatures of about 1900°F and lower. The turbine inlet temperatures of uncooled industrial gas turbines are somewhat lower.

Based on current catalyst-substrate materials technology, it appears that catalytic combustors could be designed to operate at these temperatures. At these levels, the NO_x emissions which are related directly to the combustion temperature are expected to be very low.

Little information is currently available relative to the performance and emission characteristics of catalytic combustors operating at typical gas turbine temperatures. The only known exploratory catalytic combustor tests were conducted by Engelhard and by the EPA, using a small Engelhard catalyst specimen. Preliminary evaluation and test programs have been initiated by NASA/Lewis and by the AFAPL. These programs are briefly discussed in the following sections.

4.4.4.1 Air Force Aero Propulsion Laboratory

4.4.4.1.1 Program Description

Efforts are currently under way at AFAPL to develop and evaluate gas turbine combustor modifications in an effort to reduce the CO, HC, and NO emissions from military jet aircraft. Both current and advanced technology modifications are being considered. The current technology modifications consist of minor as well as major design changes involving the combustor liner, fuel injector, and fuel-air mixing devices, and incorporation of water injection. The advanced technology modifications include variable area geometry combustors, staged fuel injection, and premixed fuel-air injection schemes. These approaches are expected to be very effective in terms of CO and HC

emission reduction, but probably will be much less effective in reducing the NO_x emissions, especially at takeoff and climb thrust levels of the engine (Ref. 4-35).

Current and projected NO_x emissions from jet engines are presented in Figure 4-20 (Ref. 4-36). Curve 1 in this figure represents current commercial and military jet engines, curve 2 is the AFAPL projection for 1979-type hardware, and curve 3 is based on modified conventional combustors plus water injection. Since the projected reductions are quite modest, AFAPL decided some time ago to search for novel combustor techniques which have the potential of significantly lower NO_x emissions. Based on these considerations, it negotiated a zero dollar contract with Engelhard covering delivery by Engelhard of a catalytic combustor that could be used by AFAPL in simulated engine test work. In return, Engelhard will receive all test data acquired in the program and will have some control regarding the publication of these data. The AFAPL test program is designed to provide fundamental performance data on the catalytic combustor under a variety of operating conditions. Currently, the program is considered to be a phase I feasibility effort which may be extended if the initial test results are favorable.

The design, fabrication, and setup of the test section illustrated in Figure 4-21 have been completed (Ref. 4-36). Current efforts are concentrated on the final development of an optimum fuel injection and fuel-air mixing scheme which is capable of providing a uniform flow velocity and mixture ratio distribution at the inlet of the catalytic combustor under all operating conditions. Compressed plant air, which is available at pressures up to 17 atm and temperatures up to 850°F , will be used in the program to simulate the operating conditions at the inlet of a typical jet engine combustor.

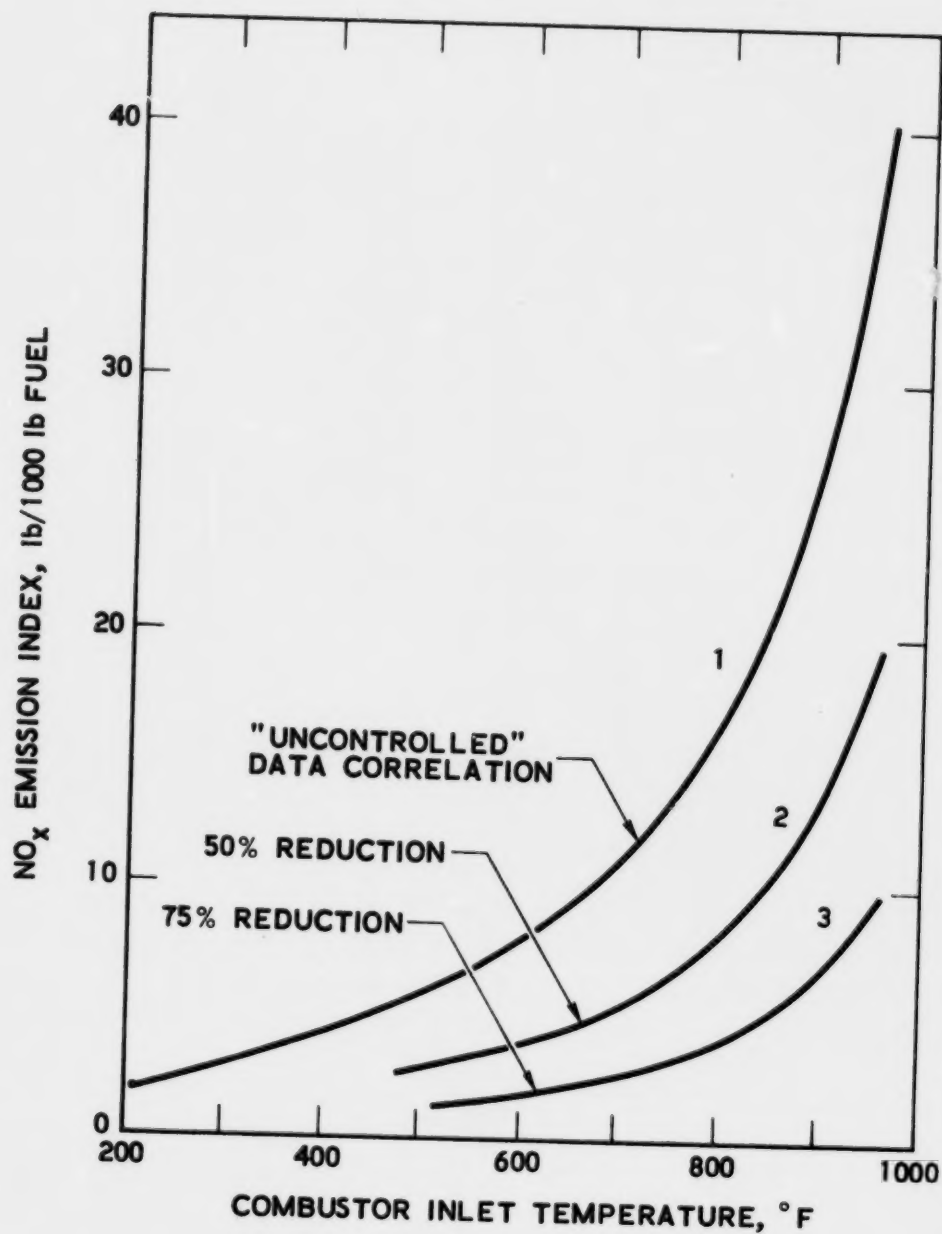


Figure 4-20. Aircraft Gas Turbine Emission Goals
(Ref. 4-35)

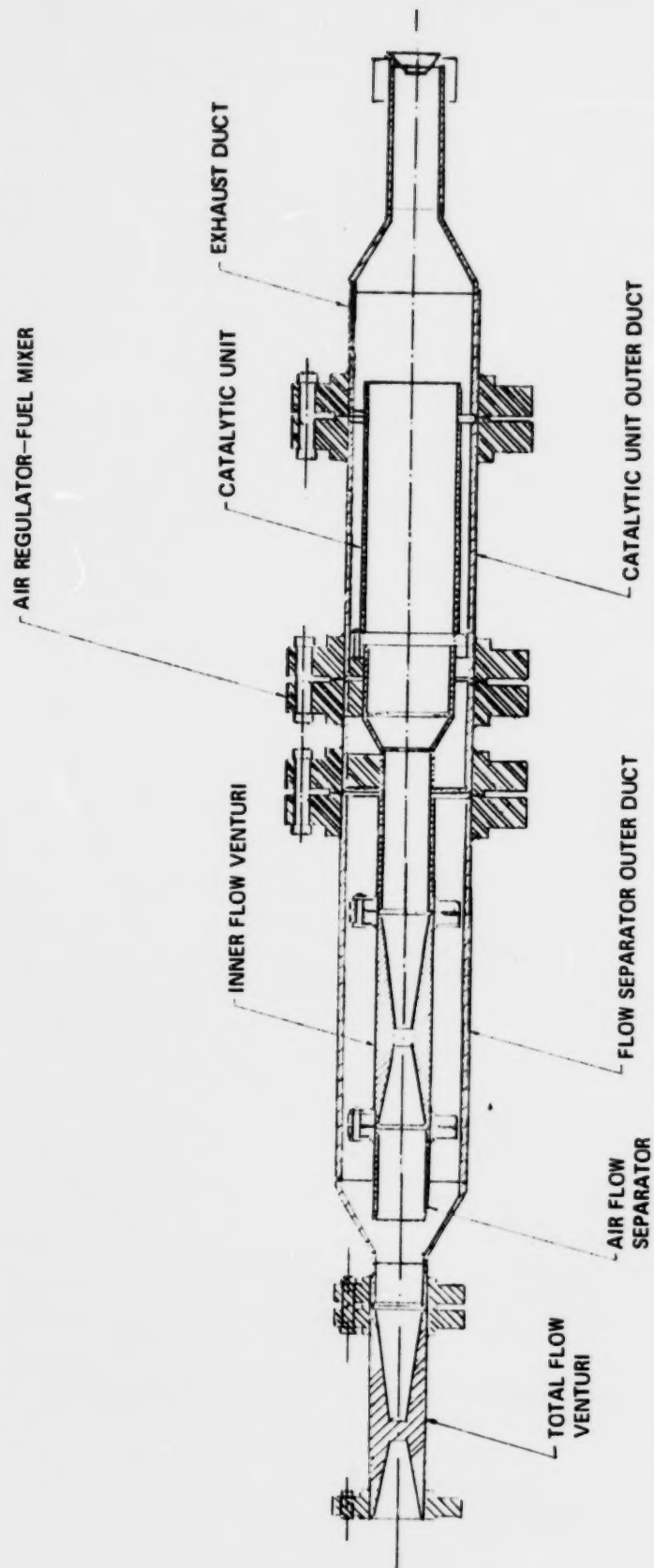


Figure 4-21. Catalytic Combustor Test Setup--Air Force Aero Propulsion Laboratory

The program is comprised of the following six tasks, which are briefly discussed in Sections 4.4.4.1.2 through 4.4.4.1.7.

1. Ignition limits
2. Heat release rates
3. Fuel vaporization effects
4. Catalyst degradation
5. Transient operating conditions
6. Emission characteristics

4.4.4.1.2 Ignition Limits

The ignition characteristics of the catalyst will be evaluated at the beginning of the test program and the optimum flow rate, air-fuel ratio, air pressure, and temperature required for lightoff will be determined. As part of this task, the feasibility of using APU exhaust gas for catalyst preheating will be also investigated.

In addition, flashback and blowoff limits of the combustor will be established for various operating conditions. To prevent flashback, AFAPL has tentatively selected a lower flow velocity limit of about 20 ft/sec. Also, screens and/or other fixes may be installed upstream of the catalyst to prevent flashback into the flow injection-mixing region of the setup.

4.4.4.1.3 Heat Release Rates

One of the most important factors affecting feasibility considerations of catalytic combustor is the maximum specific heat release rate of the unit. Obviously, this parameter has a direct impact on the size and weight of the combustor. Current jet engine combustors are designed for heat release rates of about 10×10^6 Btu/hr-ft³-atm. In the test program, the heat release rate will be varied by gradually increasing the fuel and air flow rates until a sharp rise is observed in the emissions or until other combustor performance parameters are significantly compromised.

4.4.4.1.4 Fuel Vaporization Effects

In this task, the degree of vaporization of JP-type fuels required for catalytic combustion will be evaluated. Although the test plan initially called for testing of a number of fuels, including gaseous and certain distillate fuels, the program in its present form is limited to JP fuels.

The degree of fuel vaporization will be varied by varying (1) the distance between the fuel injection points and the catalyst, (2) the air flow rate through the fuel-air mixing section, and (3) the temperature of the incoming fuel. According to AFAPL, a small amount of nonvaporized fuel might be tolerable.

4.4.4.1.5 Catalyst Degradation

The AFAPL test plan provides for a 100-hour durability test of the catalytic combustor. The objective of this test is to determine the degree of deterioration in catalyst lightoff temperature and other performance parameters such as emissions and combustion efficiency. However, the scheduled test time of 100 hours is considered insufficient to yield the information required for a comprehensive assessment of the durability characteristics of this catalytic combustor.

4.4.4.1.6 Transient Operating Conditions

This program task is concerned with the determination of the thermal shock characteristics of the catalyst/substrate materials. This will be accomplished by exposing the catalyst to rapidly changing temperature conditions of up to 500°F/sec. Vibration tests are not considered in this task.

4.4.4.1.7 Emission Characteristics

The AFAPL test plan calls for emission measurements over a wide range of simulated engine operating conditions. Air-fuel ratios will be varied between approximately 25 and 120. These values cover the range between full power and idle operation of a typical jet engine. The air pressures and inlet temperatures will be varied accordingly. For instance, engine idle will be simulated by operating the combustor at an air inlet temperature of about 350°F and a pressure of 4 atm.

The instrumentation available at AFAPL for emission measurement includes heated FID for HC, nondispersive infrared for NO and CO, and chemiluminescence for NO_x. This instrumentation is considered adequate to assure the required accuracy of the test data.

AFAPL expects low NO_x emissions from catalytic combustors because of the low flame temperatures, which result from operation of the combustor in the lean fuel-air ratio regime. Conversely, in conventional gas turbine combustors, the fuel is burned near stoichiometric in the primary zone and this results in much higher temperatures and NO_x formation rates. AFAPL feels that NO_x emission indexes (defined as lb of NO_x/1000 lb of fuel burned) below 1.0 might be achieved with catalytic combustors under all operating conditions. As shown in Figure 4-20, this would constitute a significant improvement over current combustor designs.

Idle combustion efficiencies above 99.5 percent are predicted by AFAPL for catalytic combustors. For comparison, current aircraft gas turbine engine combustors have idle efficiencies of the order of 90 to 98 percent, depending upon the particular combustor-engine configuration considered. The projected increase in combustor efficiency results in substantially lower CO and HC emissions over typical landing and takeoff duty cycles of the aircraft.

4.4.4.2 Engelhard Industries

4.4.4.2.1 Program Description

To date, most of the catalytic combustor work conducted by this company has been performed in a simulated gas turbine test rig. It is Engelhard's opinion that the data obtained from these tests are scaleable to large units. The CO and HC emissions in larger combustors should be less than those from this unit, because of the more favorable surface-to-volume ratio of the larger units. This fact results in a reduction of the quenching effects of the CO and HC oxidation reactions in the outer regions of the catalyst.

Based on an in-house feasibility study of catalytic combustion concepts, Engelhard has identified a number of potential applications. These include kitchen equipment, hot water heaters, stationary gas turbines, automotive gas turbines, and aircraft gas turbines (Ref. 4-18).

Currently, Engelhard has working agreements with a number of outside organizations, including NASA/Lewis and the AFAPL. Under the terms of these agreements, it has provided one catalytic combustor each to NASA and to AFAPL for testing by these organizations over a range of simulated gas turbine operating conditions.

All catalytic combustion work performed to date has been company-sponsored. However, negotiations regarding the development of catalytic combustors are currently being conducted with a number of gas turbine manufacturers.

To date, Engelhard has not been involved in very detailed evaluation studies of the applicability of catalytic combustors to steam boilers. In the past, the Atomic Energy Commission (AEC) had shown interest in a potassium boiler and Engelhard proposed a catalytic combustor arrangement for this application using imbedded boiler tubes. However, this concept was rejected by the AEC because it felt that the ceramic substrate would crack under the specified operating conditions. Engelhard still believes that the originally proposed concept could be developed into a viable design.

4.4.4.2.2 Test Fuels

A number of different gaseous and liquid fuels have been utilized in Engelhard's catalytic combustor test work. These fuels include pure propane, commercial propane (major constituents about 73 percent propane and 24 percent propylene), methane, low-energy coal gas (heating value approximately 120 to 160 Btu/scfm), gasoline, and diesel fuel. Unleaded gasoline has been specified by the EPA for use in its automotive gas turbine development programs. Nondistillate fuels have not yet been evaluated and Engelhard declines to make predictions regarding the use of these fuels in catalytic combustors.

4.4.4.2.3 Projected Advantages

In Engelhard's opinion, the principal advantage of the catalytic combustor concept lies in its capability of operating in the fuel-lean regime, which is not possible in the primary zones of current technology combustors. As a result, the maximum combustion temperatures will be much lower than the peak temperatures in conventional combustors; this will minimize the formation of NO_x . Furthermore, Engelhard expects high catalytic combustion efficiencies resulting in low CO and HC emissions. The organization is confident of achieving these goals with its design, but feels that a comprehensive demonstration program is mandatory before a final assessment of catalytic combustors can be made.

4.4.4.2.4 Combustor Design Features

Engelhard considers the catalyst and substrate compositions and the manufacturing processes to be proprietary information. The temperature capabilities of Engelhard's catalytic combustor designs have not yet been evaluated. Current substrate materials are limited to continuous operating temperatures of about 2400°F , but higher temperatures might eventually be feasible with advanced substrate designs. However, as the temperature is further increased, the rate of NO formation in the combustion zone increases rapidly; this would have to be weighed against the potential advantages resulting from operation at the higher combustion temperature.

The Engelhard catalytic combustors are designed for pressure drops of the order of 1 to 3 percent of the total pressure of the fuel-air mixture entering the catalyst. These values are comparable to the pressure losses of current conventional gas turbine combustors.

4.4.4.2.5 Operational Characteristics

Engelhard is currently working on the development of a number of proprietary lightoff schemes. In its opinion, different approaches might be used for the different fuels to account for lightoff temperature differences.

Preignition and flameout are two potential problem areas impacting conventional combustor designs. With regard to preignition, Engelhard feels that catalytic combustors are equivalent to other prevaporizing combustor designs currently being evaluated by the automotive and aircraft gas turbine industries. Also, flameout is not considered to be a serious problem area because the catalyst is self-igniting above the lightoff temperature.

Catalyst durability tests have been conducted on some samples for up to about 1000 hours. These tests, which were run at steady-state conditions, showed no performance degradation of the catalyst. Although these results are certainly encouraging, they are by no means adequate to predict the performance of the catalytic combustor in actual operation in a gas turbine. Engelhard has conducted some preliminary cycling tests in which the fuel flow was intermittently turned on and off. No performance degradation of the catalyst was observed during these tests.

4.4.4.2.6 Emission Characteristics

To date, Engelhard has conducted some exploratory emission test work on catalytic combustors, using gaseous fuels as well as gasoline. In these tests, the air-fuel ratio was adjusted to about 38:1 and the pressure and temperature of the incoming air was varied up to 5 atm and 500°C, respectively. These values were selected to simulate typical operating conditions of regenerated automotive gas turbines. The following average pollutant concentrations were obtained:

NO _x	undetectable
HC	less than 10 ppm
CO	less than 60 ppm

According to Engelhard, the emissions are independent of the pressure and temperature levels of the incoming fuel-air mixture.

Engelhard feels that the instrumentation and test procedures used in its experimental work are adequate to assure accurate emission data, even at the low levels typical of catalytic combustors. The instrumentation had been originally acquired for use in Engelhard's automotive catalyst development work and includes chemiluminescence for NO_x (1 to 10 ppm low scale), NDIR

for CO and CO₂, and heated FID for HC. In addition, it has a scanning electron microscope and x-ray equipment for substrate analysis.

4.4.4.2.7 Catalytic Combustor Cost

Cost data for catalytic combustors are currently not available. However, Engelhard states that it must be competitive with other gas turbine combustor configurations. For comparison, Engelhard indicated that the cost of a PTX oxidation catalyst delivered to the automobile manufacturer is less than \$50, and only a small fraction of that amount is for the catalyst material itself. To minimize cost, the platinum group metals could be reclaimed economically if such metals would be used in catalytic combustors.

According to Engelhard the catalytic combustors could be manufactured in its existing catalyzing facilities. It would probably not be interested in the manufacture of complete catalytic combustor units, but would supply catalyzed substrates to the gas turbine manufacturers.

4.4.4.3 EPA, Control Systems Laboratory

4.4.4.3.1 Program Description

An exploratory test program was conducted by the Control Systems Laboratory of the EPA using a high temperature catalytic converter provided by Engelhard Industries (Ref. 4-19). This unit was designed by Engelhard for operation up to 2400°F. In the EPA tests, the combustor was operated with premixed propane-air mixtures uniformly distributed over the inlet of the combustor. The catalyst temperature was varied between 1800°F and 2300°F by varying the air-fuel mixture ratio. The lower temperature limit was selected to prevent combustion instability.

4.4.4.3.2 Emission Characteristics

The test data from the program indicate NO_x emissions less than 10 ppm at all operating conditions. Considering the reduced accuracy of the NDIR instrument at this low concentration level and the fact that the laboratory air

contained about 4 to 8 ppm NO_x, the NO_x emissions of the catalytic burner are very low indeed. The HC emissions are also extremely low. Because of instrumentation problems, CO emissions were not reported by EPA. However, there is evidence that the CO concentrations are also low.

In a final test series, approximately 65 ppm NO was added to the combustor inlet air. Under these conditions, the average NO_x concentration at the combustor exit was about 70 ppm, indicating essentially zero NO_x conversion efficiency. Considering the lean fuel-air mixture used in these tests and the associated NO_x reaction kinetics, this result is not too surprising.

4.4.4.4 NASA/Lewis

4.4.4.4.1 Program Description

NASA/Lewis is currently involved in several gas turbine programs in which catalytic combustors are being considered. These efforts are primarily in support of the Advanced Automotive Power Systems Program of the EPA and include development and test work related to a catalytic combustor designed for use in the Chrysler automotive gas turbine which is currently being developed with EPA funding. In addition, NASA/Lewis is evaluating catalytic combustors for a number of other potential applications, including stationary and aircraft gas turbines (Ref. 4-37).

As part of EPA's gas turbine program, NASA/Lewis will run tests on a catalytic combustor designed and manufactured by Engelhard Industries. The composition of the catalyst and the substrate materials used are proprietary to Engelhard. Initial performance and emission tests are scheduled to commence in May 1973, covering the following ranges of operating conditions:

air-fuel ratio	25 to 100
air inlet temperature	400 to 1000°F
air inlet pressure	2 to 6 atm
catalyst through-flow velocity	20 to 100 ft/sec

NASA recognizes that a uniform air-fuel mixture and mass distribution is required at the catalyst inlet to prevent catalyst failure due to overtemperature. If liquid fuels are used, the fuel must be prevaporized. The degree of vaporization required for satisfactory catalyst operation is currently not known and will be determined experimentally. To provide a high degree of vaporization, NASA is currently running tests on a small swirl-type injector configuration which is designed to provide a well-mixed, prevaporized fuel-air mixture at the inlet to the catalyst. This type of injector-mixing chamber is being also considered by NASA for use in advanced jet engine combustors.

Durability testing of catalytic combustors will be conducted by NASA upon completion of a screening test program currently under way at Engelhard. In the Engelhard tests, different catalyst-substrate samples will be screened and the two best designs will then be selected for the NASA durability program.

NASA's current plans are to conduct a very extensive test program on catalytic combustors in order to acquire all the data needed for a meaningful assessment of this concept.

4.4.4.4.2 Operational Characteristics

NASA states that the catalytic combustor will be preheated electrically or by means of waste heat from auxiliary power units or other sources. In any case, no startup problems are foreseen.

With regard to emissions, NASA expects very low CO, HC, and NO_x concentrations in the combustor exhaust.

4.4.4.4.3 Cost Data

At this time, NASA has no cost data for catalytic combustors. Upon completion of its feasibility test program, it will initiate a thorough economic analysis of catalytic combustors as well as porous-plate type combustors. NASA's current opinion is that catalytic combustors might be somewhat more costly than equivalent porous-plate designs.

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SECTION 5

EVALUATION OF POROUS-PLATE AND CATALYTIC SURFACE COMBUSTORS FOR LARGE UTILITY BOILERS

5.1 POROUS-PLATE SURFACE COMBUSTORS

5.1.1 Introduction

The basic features and operating principles of porous-plate surface combustion for use in Rankine or Brayton cycle power plants can be most easily described in terms of a schematic of a typical porous-plate burner as shown in Figure 3-7. Premixed fuel and air passes through the porous matrix at low velocity and burns in a flat, thin (approximately 1 mm thick) laminar flame positioned close to the porous burner surface. Because of the close proximity of the flame to the surface, an appreciable amount of heat is transferred from the burner gases to the porous surface by convection and radiation. The heat is then removed from the porous matrix, either by cooling tubes imbedded in the plate and/or radiation from the burner surface. The removal of this heat reduces the temperature of the burned gases below the adiabatic flame temperature. Since the magnitude of the NO_x emissions is highly dependent on the maximum flame temperature, this approach offers the possibility of achieving low NO_x emissions. This is shown in Figure 5-1. As indicated, a temperature reduction from 2200°K to 2000°K reduces the NO_x formation rate by a factor of about 20. Peters (Ref. 5-1) has demonstrated in small-scale porous-plate combustors that the NO_x emissions can be reduced in this manner. However, to date, no one has seriously examined the application of porous-plate surface combustors to large utility boilers. While the porous plate is a convenient way of removing heat from the combustion zone, it is possible that better approaches might be devised.

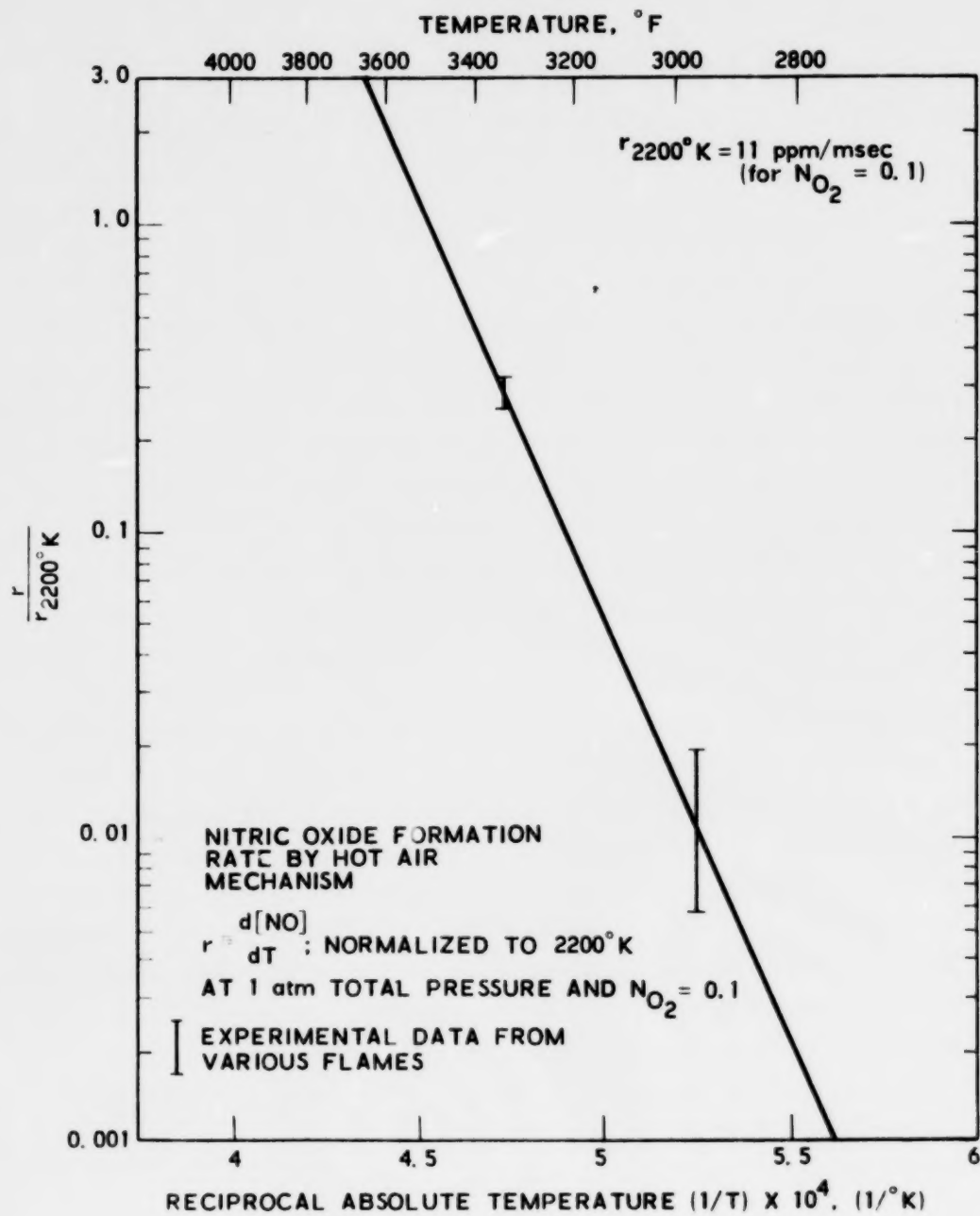


Figure 5-1. NO Formation Rate

The objective of this section is to (1) briefly evaluate the potential of liquid-cooled, porous-plate surface combustors in reducing the NO_x emissions from large utility boilers, and (2) determine the most critical research work needed to permit its early application. The evaluation will be carried out by setting up low NO_x emission design goals for a typical large utility boiler and determining if a porous-plate combustor can be reasonably expected to satisfy the postulated requirements.

5.1.2 NO_x Emission Level Target

There is no apparent reason, other than achieving lower NO_x emission levels, to consider the use of porous-plate surface combustion in large utility boilers. Hence, the target NO_x emission should be set appreciably lower than is currently obtainable with the best existing or projected abatement approaches. For comparison, the NO_x emissions projected for the Scattergood No. 3 unit of the Los Angeles Department of Water and Power are shown in Figure 5-2 (Ref. 5-2). This unit has lower projected NO_x emissions than any other large utility boiler in the United States. It has a capacity of 460 MW, but will be restricted in output to 315 MW by Rule 67 of the Los Angeles Air Pollution Control District. This rule limits the NO_x emissions of an individual point source to 140 lb/hr in order to maintain acceptable local NO_x concentrations. At 315 MW, the corresponding NO_x emissions are 42 ppm. To ensure NO_x emissions appreciably lower than those provided by the existing technology, the NO_x emission target goal for this study has been set in the 10 to 20 ppm range.

5.1.3 Boiler Design Requirements

5.1.3.1 Porous-Plate Surface Combustor Operating Conditions

In order to achieve low HC and CO emissions while maintaining high boiler efficiency, the surface combustor must operate at fuel-air equivalence ratios of slightly less than unity. Currently, no NO_x emission data are available for this equivalence ratio at sufficiently low gas temperatures to achieve the desired target emissions. However, it is apparent from Figure 5-3 (Ref. 5-2), which presents the NO_x emissions for an equivalence

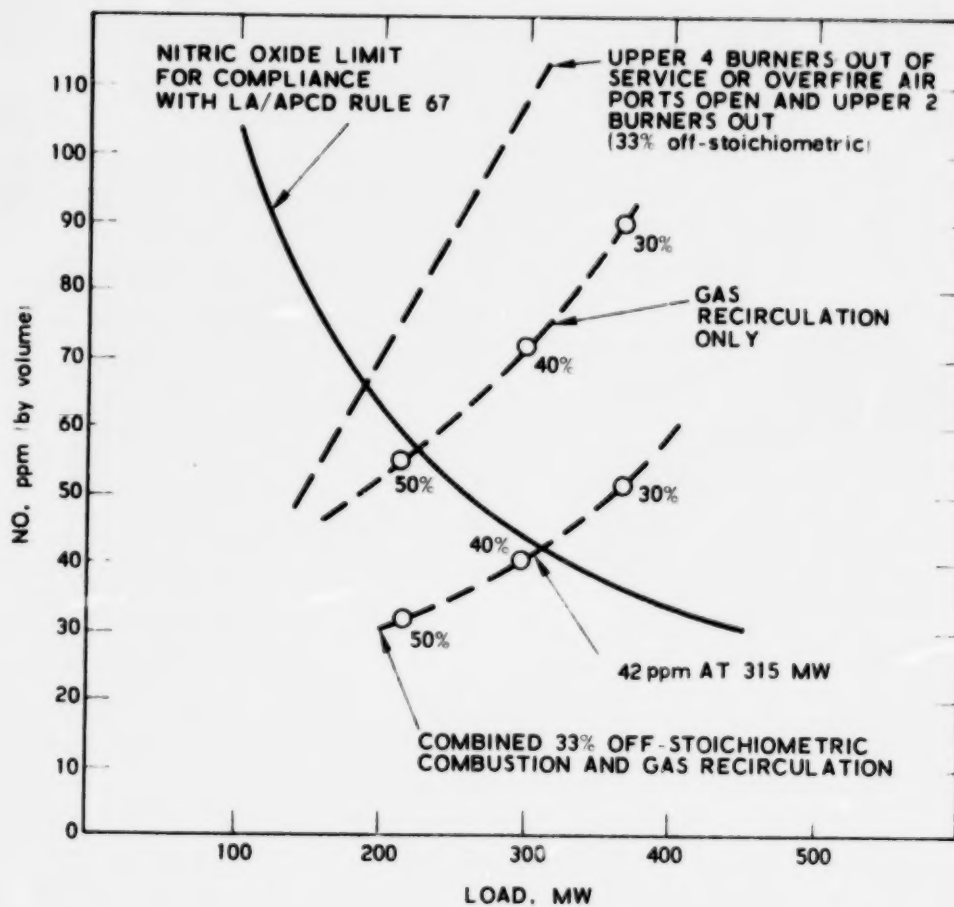


Figure 5-2. Predicted NO_x Emissions vs Mode of Operation for Scattergood No. 3 Unit (Ref. 5-2)

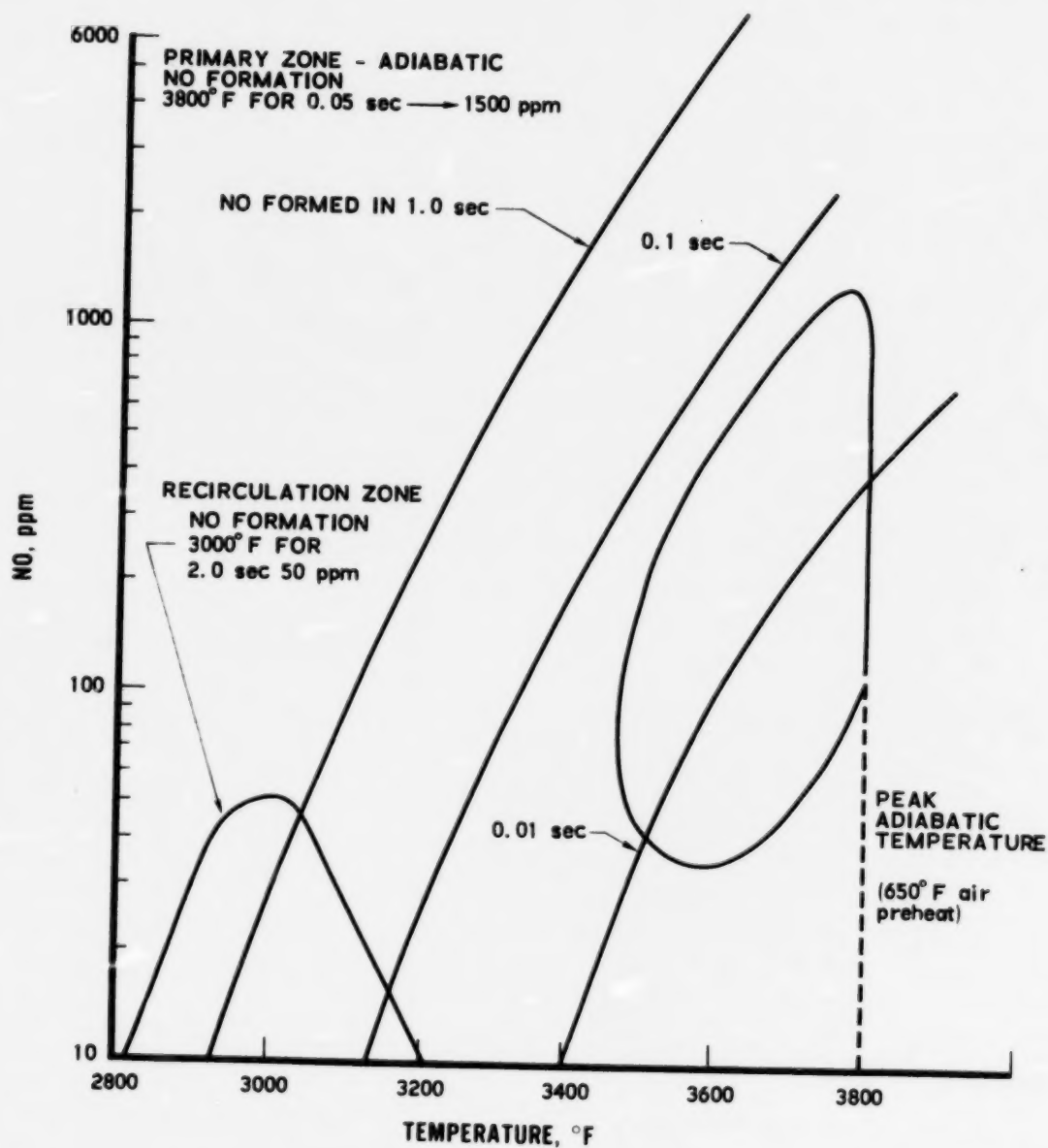


Figure 5-3. Kinetic NO Formation for Combustion of Natural Gas at Stoichiometric Mixture Ratio--Atmospheric Pressure

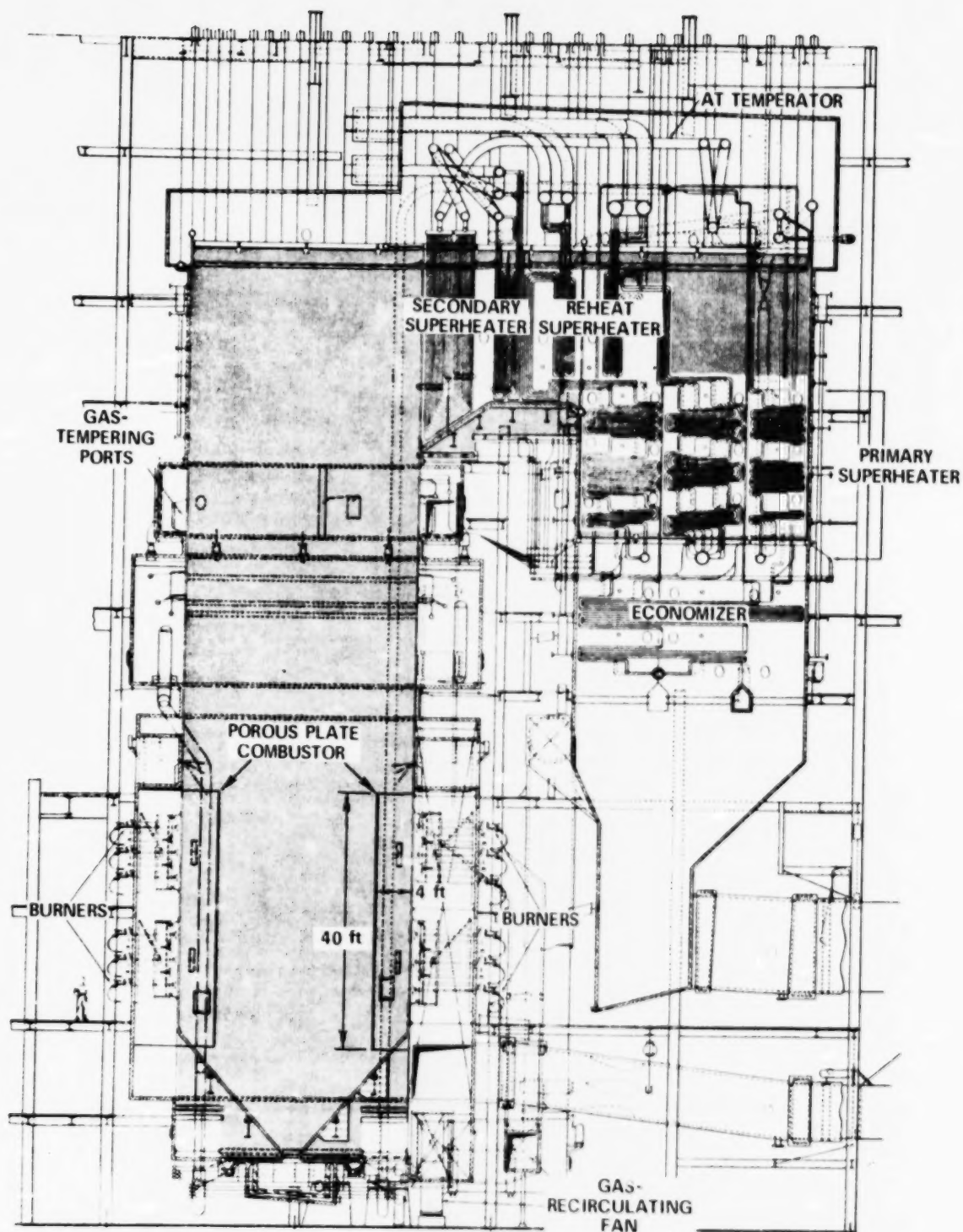


Figure 5-4. Haynes Supercritical Steam Boiler--
Units 5 and 6

ratio of 1.0, that NO_x concentrations of 10 ppm can be achieved for gas temperatures of 3000°F and residence times of a few tenths of a second. The general trend of the NO_x emissions with increasing excess air is shown in Figure 3-2 (Ref. 5-3). As indicated, at a few percent excess air the NO_x emissions will be somewhat higher than 10 ppm, but still appreciably below the lowest projected value of 42 ppm. Therefore, a gas temperature of 3000°F and a residence time of a few tenths of a second will be taken as the design condition for the porous-plate surface combustor considered in this study.

5.1.3.2 Fuel

Because of the small pore size of porous-plate surface combustors, (e.g., the burner design in Ref. 5-4 has a pore size of 250 microns), only gaseous fuels or distillate fuels that can be readily prevaporized are considered as candidate fuels for porous-plate surface combustors. The evaluation has been made using natural gas, which is by far the most popular and available gaseous fuel for large utility boilers. Distillate fuels have not been economically competitive with other fuels for this application. Methane, which is the main constituent of natural gas, has been selected as the fuel for this analysis.

5.1.3.3 Utility Boiler Type and Size

Because the present shortage of natural gas may severely limit new gas-fired utility boiler plant construction, the application selected for this evaluation is the retrofitting of an existing boiler. More specifically, retrofitting of units 5 and 6 of the Haynes Steam Plant of the Los Angeles Department of Water and Power has been selected for the evaluation example. The important boiler characteristics for these units are shown in Table 5-1 and the boiler is illustrated in Figure 5-4.

Table 5-1. Characteristics of Existing Boiler for Units 5 and 6 of Haynes Steam Plant (Los Angeles Department of Water and Power)

Maximum gas flow rate	2,760,000, scfm
Number of burners	24
Dimensions of boiler (approx.)	25 × 25 × 120 ft
Burner arrangement	4 vertical rows over 26 ft elevation, 12 burners on front and 12 on rear wall
Air preheat temperature	650°F
Temperature at entrance to secondary superheater	2500°F

Porous-plate surface combustors require a large surface area, because the laminar flame speeds are very low, which leads to large burner volume requirements. In general, volume constraints are more critical in the retrofitting of existing boilers than in new boiler designs. Hence, if an existing boiler can be retrofitted, there should be no volume constraint problem with the new design.

5.1.4 Burner Characteristics

5.1.4.1 Burner Surface Area

The required burner surface area may be determined from the following equation

$$A = \frac{Q (1 + a/f)}{\rho u h_v} \quad (1)$$

where

A = required burner surface area

Q = rated heat input to the boiler

ρ = density of the air-fuel mixture on the cold side of the burner

u = flame speed on the cold side of the burner

a/f = air-fuel ratio of the burner

h_v = fuel heating value

The mass velocity ρu may be determined from the continuity equation

$$\rho u = \rho_{25} u_{25} \quad (2)$$

where subscript 25 denotes 25°C. Kaskan (Ref. 5-5) has determined u_{25} for a large number of gaseous fuels; his results for methane are shown in Figure 5-5. As indicated in this figure and from Eq. (1), the required burner surface area increases rapidly with decreasing gas temperature. For Haynes units 5 and 6, the required burner surface area is approximately 21,000 ft² for a maximum gas temperature of 3000°F and an equivalence ratio of unity. This area is somewhat larger than the water wall area of the Haynes boiler. Reducing the gas temperature to 2500°F would increase the required burner surface area approximately fourfold.

5.1.4.2 Burner Configuration

Many different porous-plate burner configurations might be feasible. However, the configuration chosen should satisfy the following requirements:

1. To minimize the required burner surface area, the gas temperature immediately downstream of the porous-plate surface should be as high as possible consistent with the desired NO_x emission level.
2. To avoid a major boiler rebuild, the porous-plate burner must be designed to fit the existing boiler envelope, and the gas temperature entering the secondary superheater should be about 2500°F, matching the temperature of existing boilers.

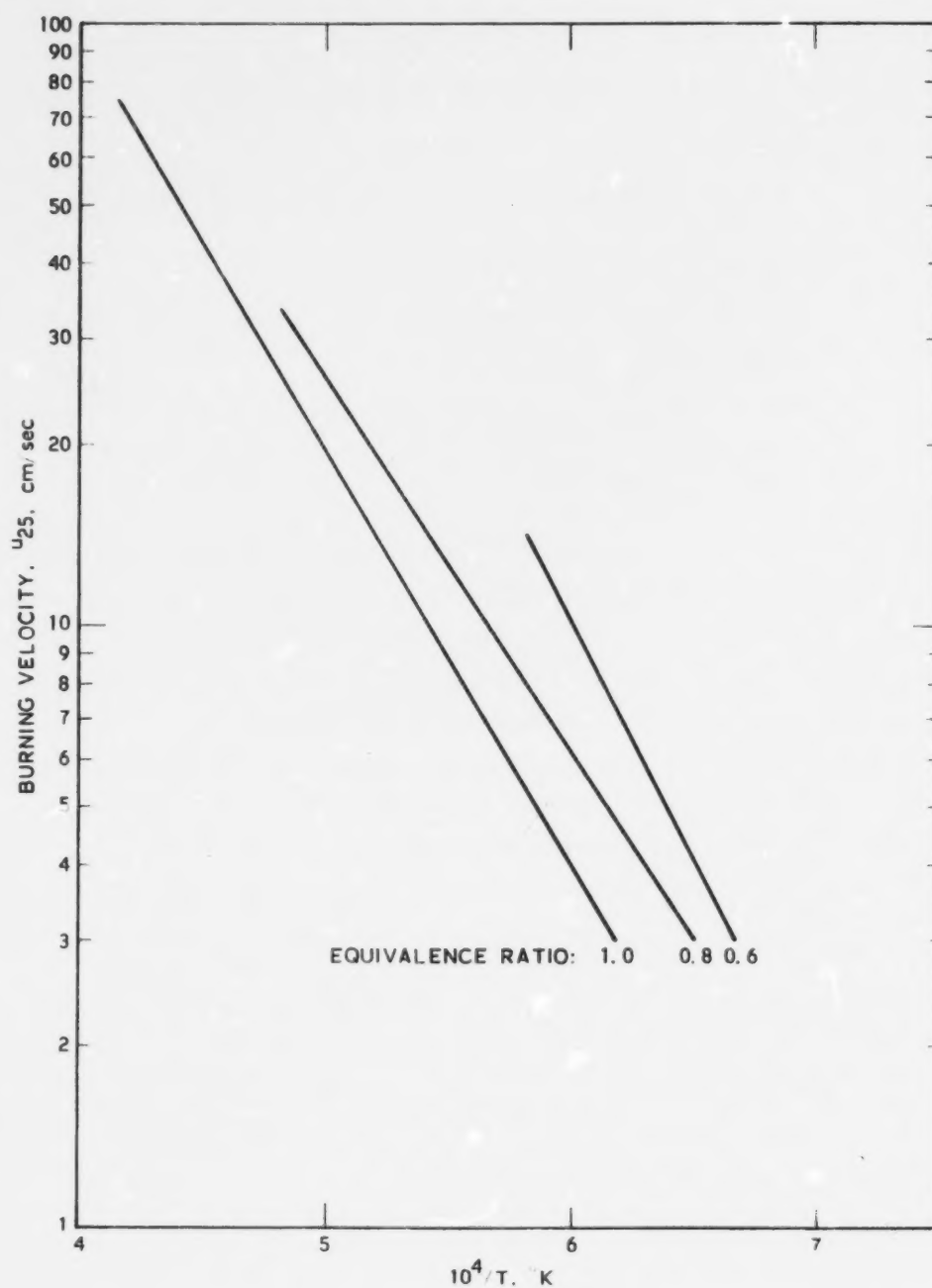


Figure 5-5. Burning Velocities of Methane-Air Mixtures vs Reciprocal Temperature (Ref. 5-5)

3. To minimize plant modification cost, maximum use should be made of the existing water wall to reduce the burner gas temperature to the level required at the entrance to the secondary superheater.
4. To achieve the desired residence time of a few tenths of a second, the burned gases must be quickly accelerated after leaving the burner surface and directed to a location where rapid cooling takes place by means of forced convection or radiation.

A configuration which attempts to satisfy these requirements is shown in Figures 5-4 and 5-6. In this design, the burner covers the full width of the boiler which, in the case of the Haynes boiler, is about 25 ft. The gas flow arrangement is adapted from that shown in Figure 3-10 (Ref. 5-4).

The principal uncertainty regarding the design shown in Figure 5-6 is the fact that a high burned gas velocity of approximately 100 ft/sec is required parallel to the porous-plate surface. To date, the effects of a high cross-velocity on burner performance have not been thoroughly evaluated. General Electric (Ref. 5-6) has successfully operated with cross-velocities up to 200 ft/sec using a wire screen between the burner surface and the high velocity cross-flow. However, this approach is considered impractical at the gas temperatures used in this example, unless the screen were water-cooled; this would cause a very sizable increase in complexity and volume of the burner. Bone (Ref. 5-7) does not explicitly state the cross-velocity in his porous-plate combustor boiler tests, but it can be inferred from the stated burner dimensions and the laminar flame speed that the cross-velocity was of the order of 80 ft/sec. Hence, it is believed that 100 ft/sec, while not demonstrated, is probably achievable.

5.1.4.3 Cooling Requirements

The heat Q_c that must be removed from the porous-plate burner in order to achieve the desired gas temperature may be calculated from the following equation

$$\frac{Q_c}{A} = \rho_{25} u_{25} (H_a - H) \quad (3)$$

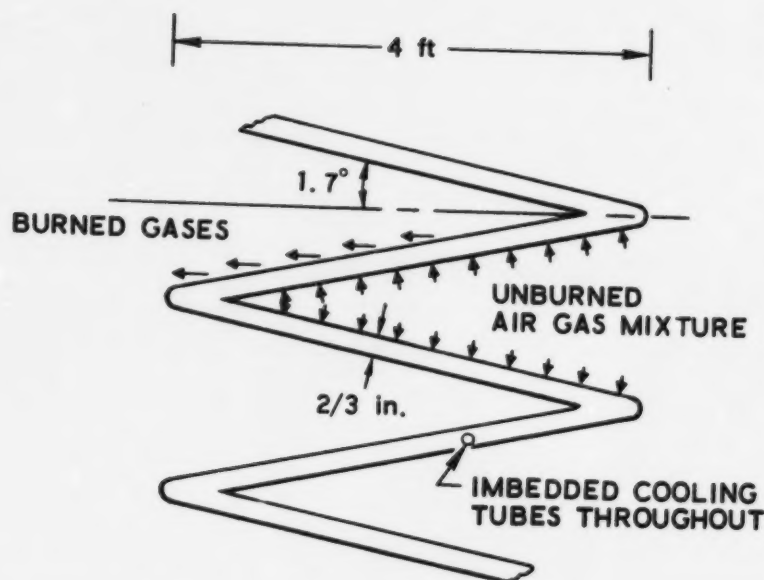


Figure 5-6. Porous Plate Burner Configuration Schematic

H_a is the enthalpy of the burned gases for adiabatic combustion, and H is the enthalpy of the burned gases at the actual gas temperature. The cooling load Q_c/A , computed for an equivalence ratio of 1.0 and a pressure of 1 atm, is depicted in Figure 5-7 as a function of gas temperature. As indicated, for a gas temperature of 3000°F the cooling load is $45,000 \text{ Btu/hr-ft}^2$, which is approximately one-third of the total burner heat release rate.

5.1.4.4 Materials Requirements

Different materials have been applied by various investigators for water-cooled porous-plate surface combustors. For example, sintered copper was used by Kaskan (Ref. 5-5) and oilite and sintered stainless steel by Peters (Ref. 5-1). No serious material problems were encountered by these investigators. However, in all these tests the burner was operated without air preheat and the average cooling water temperature was somewhat lower than would be experienced in a utility boiler application. The

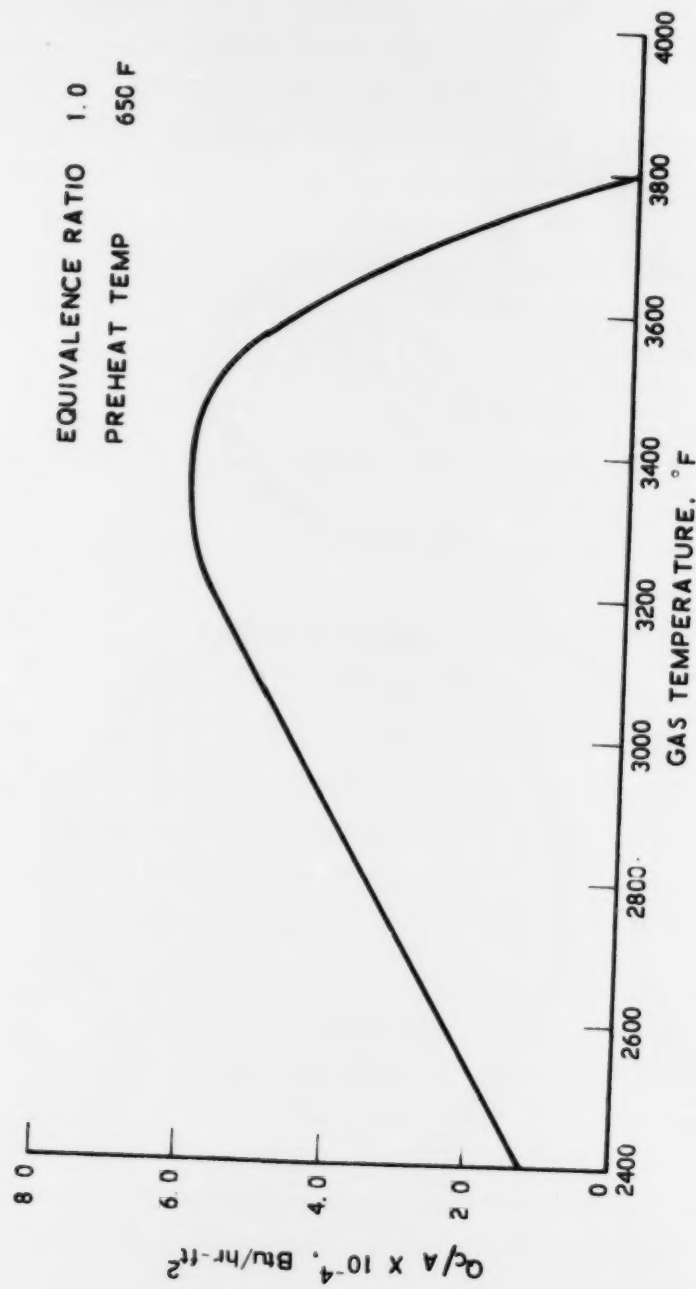


Figure 5-7. Computed Heat Flux to the Porous Plate Burner as a Function of Burning Velocity

effect of air preheat and higher water temperatures is to increase the material temperatures by several hundred degrees over present experience. However, based on the test data by Peters (Ref. 5-1), no serious materials problems are anticipated. For the oilite plate, Peters' data indicate material temperatures below 500°F in the center of the porous plate and the surface temperature is expected to be only slightly higher. Even if the surface temperature were increased by several hundred degrees, the oilite material would still perform satisfactorily. However, more detailed calculations are required before an accurate evaluation of the temperature conditions of the plate can be made.

5.1.4.5 Steam Rate Control

In order to maintain maximum boiler efficiency at reduced power plant load, it is desirable always to operate the boiler at an equivalence ratio near unity and with preheat. Since the burner flow velocity u depends only on equivalence ratio and burner inlet air temperature, the boiler output can only be lowered by reducing the burner surface area. This can be accomplished by shutting down sections of the burner.

5.1.4.6 Other Considerations

Because of the extremely small pore size of the porous-plate burner (of the order of 250 micron) and the long maintenance-free service life requirement, pore-clogging due to particulate matter contained in the combustion air present a potential problem area for utility boiler applications.

The Los Angeles Department of Water and Power operates its utility boilers on natural gas in the summer when photochemical smog reaches its peak, and on low-sulfur fuel oil in the winter to reduce costs and reduce the demand for natural gas at a time when it is needed for home heating. The porous-plate burner previously discussed is not capable of running on fuel oil, although it may be possible to modify it to permit operation on either fuel (e.g., by having separate burners for natural gas and fuel oil or by using folding porous-plate burners).

5.1.5

Conclusions

1. No information is currently available regarding the application of surface combustors to large utility boilers.
2. Theory and limited small-scale burner experiments indicate that porous-plate surface combustors have the potential of achieving NO_x emission levels appreciably lower than those obtained in the best current state-of-the-art large utility boilers.
3. Porous-plate surface combustors might be feasible for existing boilers, as well as new boiler installations.
4. Porous-plate surface combustors are limited to gaseous or distillate fuels. Current shortages of these fuels may limit interest in porous-plate surface combustors.
5. Before a complete assessment of porous plate surface combustors can be made, a substantial amount of research and development is required in the following areas:
 - a. Demonstration of satisfactory operation of the burner with high exhaust velocities parallel to the porous plate surface.
 - b. Demonstration of burner operation for long periods of time in an environment typical of large utility boilers, without clogging the pores.

5.2

CATALYTIC COMBUSTORS

For efficiency reasons, utility boilers are limited to near-stoichiometric operation combined with substantial air preheat. Under these conditions, the combustion temperatures in existing natural gas-fired boilers are of the order of 3800°F with NO_x emissions varying between about 200 and 700 ppm, depending upon the particular design of the boiler. Theoretically, the NO_x emissions from these plants could be almost completely eliminated through the use of catalytic combustors, which would be designed to operate at a temperature (1) low enough to limit the formation of NO and to assure adequate service life, and (2) high enough to provide adequate CO and HC control.

Currently, commercially available catalyst substrates are limited to a maximum safe operating temperature of about 2400°F. Although the temperature capability and formulations of the active catalyst materials are considered proprietary by the catalyst manufacturers, there are indications that some catalysts might be able to maintain adequate effectiveness at these temperatures over extended periods of time. It is conceivable that other monolithic or pellet type catalysts could be developed for use at even higher temperature levels.

During the course of this study no concrete information was uncovered regarding the applicability of catalytic combustors to steam boilers, although Engelhard has briefly looked at its feasibility for a potassium boiler. The feasibility of catalytic combustors for steam boilers has been examined as part of this study; two conceptual designs, uncooled and internally cooled, were reviewed.

In the uncooled catalytic combustor design, a conventional monolithic or pellet type catalyst would be operated in the lean regime to limit the combustion temperature to the maximum allowable level, say 2400°F. This could be accomplished by using all the air and only part of the fuel in an initial catalyst stage. Upon leaving the catalytic combustor, a portion of the combustion heat would be transferred from the combustion gases to the water wall before these gases enter the mixing chamber of a second catalytic combustor stage; at this point, additional fuel would be added to raise the temperature of the combustion products to the first-stage level. The process is then repeated until all fuel is burned.

Although basically feasible, this particular approach is complex and has severe limitations as far as incorporation into existing power plants is concerned. In current boiler designs, a substantial part of the heat transfer into the water wall is accomplished by means of radiation. Since the gas temperature in catalytic combustors is limited to about 2400°F, the radiative heat transfer is rather low and thus convective heat transfer would be required to heat the water wall. As a result, the water wall would have to be completely redesigned, and the rise of pressure across the blower would

have to be increased to compensate for the higher pressure losses associated with convective heat transfer.

In the internally cooled approach, cooling tubes would be imbedded in the catalyst in order to transfer a portion of the heat of combustion into the coolant by means of conduction through the substrate. As a result, the air-fuel mixture supplied to the catalytic converter might be enriched somewhat, compared with the uncooled design, with a consequent reduction of the required catalyst volume. However, this design approach creates thermal stress problems that might be beyond the capability of ceramics; a cracking of the unit could result. Utilization of sintered metals might offer an acceptable alternative as a substrate material for internally cooled catalytic combustors, although currently these materials are limited to about 2000°F. In any case, incorporation of this concept would require a major boiler redesign effort.

Like the previously discussed porous-plate combustors, catalytic combustors require gaseous or prevaporized, premixed distillate fuels to prevent fuel coking or overtemperature conditions which might lead to catalyst deactivation or melting of the substrate material. A discussion of catalyst requirements, potential problem areas, and uncertainties is presented in Section 6.

Based on these considerations, it is unlikely that catalytic combustors could be incorporated into existing power plants, but the concept might well be feasible for new power plant designs. However, comprehensive preliminary design study efforts are required before a meaningful assessment can be made.

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SECTION 6

EVALUATION OF CATALYTIC AND NONCATALYTIC SURFACE COMBUSTION CONCEPTS FOR STATIONARY GAS TURBINES

6.1 GENERAL CONSIDERATIONS

For the past several years, gas turbines have been used extensively by the electric power utilities to supplement the power output of steam plants during periods of high demand. Other gas turbine applications include compressor drives for the petroleum and natural gas industries, total energy systems for institutional facilities and shopping centers, and continuous power generation for small utilities. In the main, these units are powered by simple-cycle (nonregenerative), dual-shaft gas turbines designed for pressure ratios between about 12 and 18 and maximum turbine inlet temperatures between 1400°F and 1800°F. In general, these engines consist of a high-pressure turbine driving the compressor and a low-pressure turbine providing power to the electric generator. The thermal efficiency of current simple-cycle gas turbines is of the order of 25 percent, which is rather low compared with the efficiencies of about 40 percent achieved in steam power plants. Because of the low thermal efficiency capability of the current state-of-the-art gas turbines, the utilities have shown little interest in these engines for large base power generating installations, except when used in combined gas turbine/steam turbine installations. In these systems, the waste heat in the gas turbine exhaust is recovered to generate steam for use by the steam turbine.

The thermal efficiency and specific fuel consumption of gas turbine engines can be substantially improved by increasing the turbine inlet temperature and/or by incorporating a regenerator. In this regenerator, a portion of the thermal energy of the turbine exhaust gases is extracted and transferred to the "cold" side of the unit in order to raise the temperature of the compressor discharge air. As a result, less fuel is required in the combustor to reach the desired turbine inlet temperature.

Higher turbine inlet temperatures require the application of improved turbine blade and rotor materials such as high nickel content alloys or even ceramics, combined with advanced turbine blade cooling techniques. Cycle temperatures as high as 3000°F are projected by several organizations for the 1980 time period (Refs. 6-1 and 6-2).

6.2

GAS TURBINE OPERATING CHARACTERISTICS

The predicted performance of current and advanced state-of-the-art simple-cycle and regenerative-cycle gas turbines is presented in Figures 6-1 and 6-2 over a range of engine operating conditions. (Ref. 6-1).

In this context, the regenerator effectiveness is defined as the ratio of the heat transferred from the "hot" turbine exhaust side to the "cold" compressor discharge side divided by the amount of heat that could be theoretically transferred. As illustrated in Figures 6-1 and 6-2, the gas turbine thermal efficiency, which relates the work output of the engine to the total energy input, increases with increasing turbine inlet temperature.

In simple-cycle gas turbines, the optimum pressure ratio increases substantially with increasing turbine inlet temperature. For instance, for a turbine inlet temperature of 1800°F, the optimum pressure ratio is about 18:1 and the cycle efficiency is approximately 30 percent. At 3000°F, the optimum simple-cycle pressure ratio increases to over 30:1. The corresponding cycle efficiency is of the order of 40 percent, which is comparable to the efficiency of current steam power plants.

Substantially higher thermal efficiencies can be achieved at much lower cycle pressure ratios by means of regeneration. According to Figure 6-2, the thermal efficiency of current steam power plants can be matched with regenerative gas turbines operating at a turbine inlet temperature of about 2000°F and a regenerator effectiveness of 90 percent. Under these conditions, the optimum pressure ratio is only about 4:1.

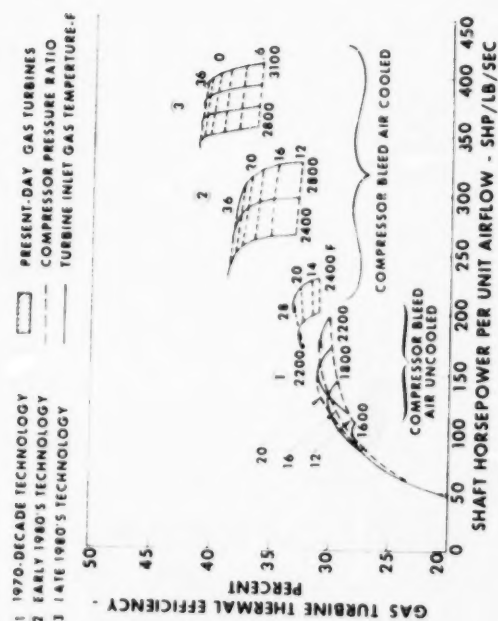


Figure 6-1. Performance Characteristics of Simple-Cycle Gas Turbines (Ref. 6-1)

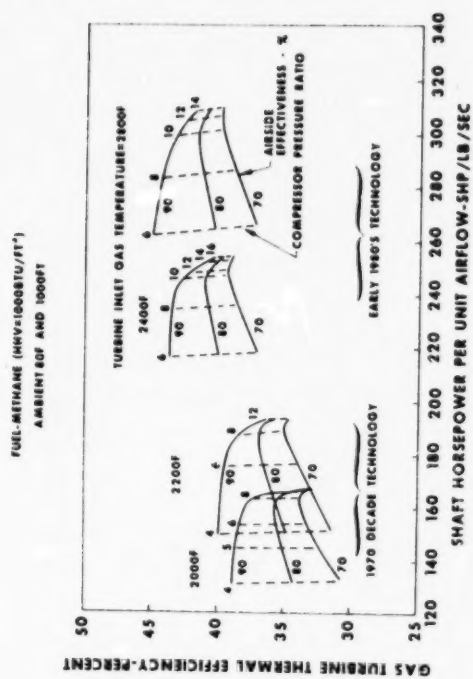


Figure 6-2. Performance Characteristics of Regenerative-Cycle Gas Turbines (Ref. 6-1)

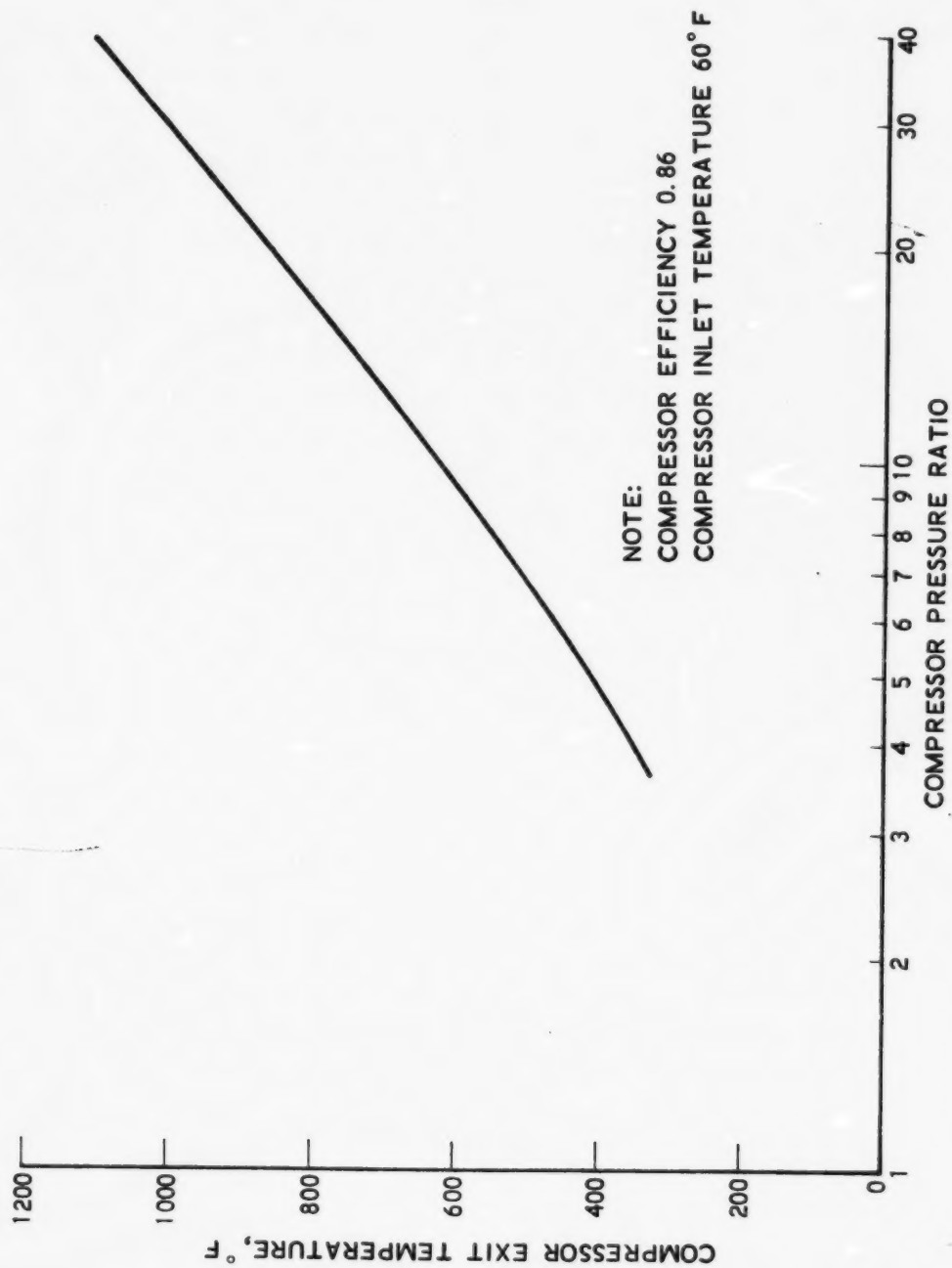


Figure 6-3. Simple-Cycle Gas Turbine Combustor Inlet Temperature vs Compressor Pressure Ratio

To permit a more meaningful feasibility evaluation of catalytic and porous-plate combustors in gas turbine applications, the combustor inlet air temperatures and air-fuel equivalence ratios were computed over wide ranges of engine operating conditions. It is well recognized that the ignition characteristics of fuel-air mixtures are strongly impacted by these two factors. A more detailed discussion of the ignition and preignition phenomena of pre-vaporized, premixed fuel-air mixtures is presented in Section 6.5.

Predicted combustor inlet temperatures for simple-cycle gas turbines are presented in Figure 6-3 as a function of compressor pressure ratio. The data are based on a compressor efficiency of 86 percent, a turbine efficiency of 88 percent, and an ambient temperature of 60°F. For the region of interest, the combustor inlet temperature of simple-cycle gas turbines varies between about 750°F and 1000°F.

The combustor inlet temperatures of regenerative-cycle gas turbines are depicted in Figures 6-4 and 6-5 for regenerator effectiveness values of 90 percent and 70 percent, respectively. Because of the high degree of regeneration and the low cycle pressure ratio, the temperatures are substantially higher than those of simple-cycle gas turbines. The curves of Figures 6-4 and 6-5 are based on the same turbomachinery efficiencies used in the simple-cycle calculations and a combined regenerator and combustor pressure loss of 4 percent of the compressor discharge pressure.

Predicted air-fuel ratios for natural gas are presented in Figure 6-6 for both simple-cycle and regenerative-cycle gas turbines. As expected, the required air-fuel ratio decreases with increasing turbine inlet temperature and decreasing degree of regeneration.

6.3 GAS TURBINE EMISSIONS

NO_x and CO mass emission test data from a number of aircraft and industrial gas turbine engines are presented in Table 6-1 in terms of pollutant concentration and pounds of pollutant per megawatt output. Also listed in this table are emission indexes computed from initial test data published by

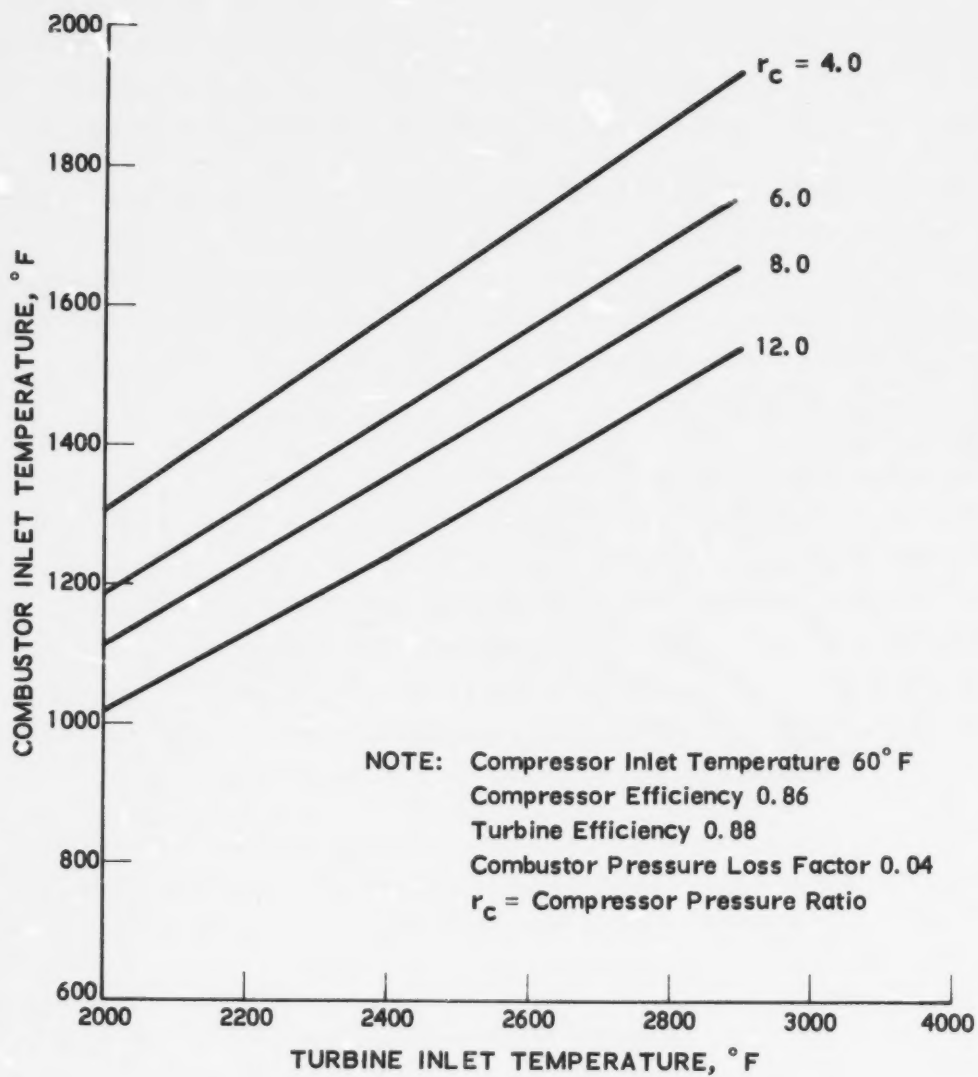


Figure 6-4. Regenerative-Cycle Gas Turbine Combustor Inlet Temperature vs Turbine Inlet Temperature-Regenerator Effectiveness 0.90

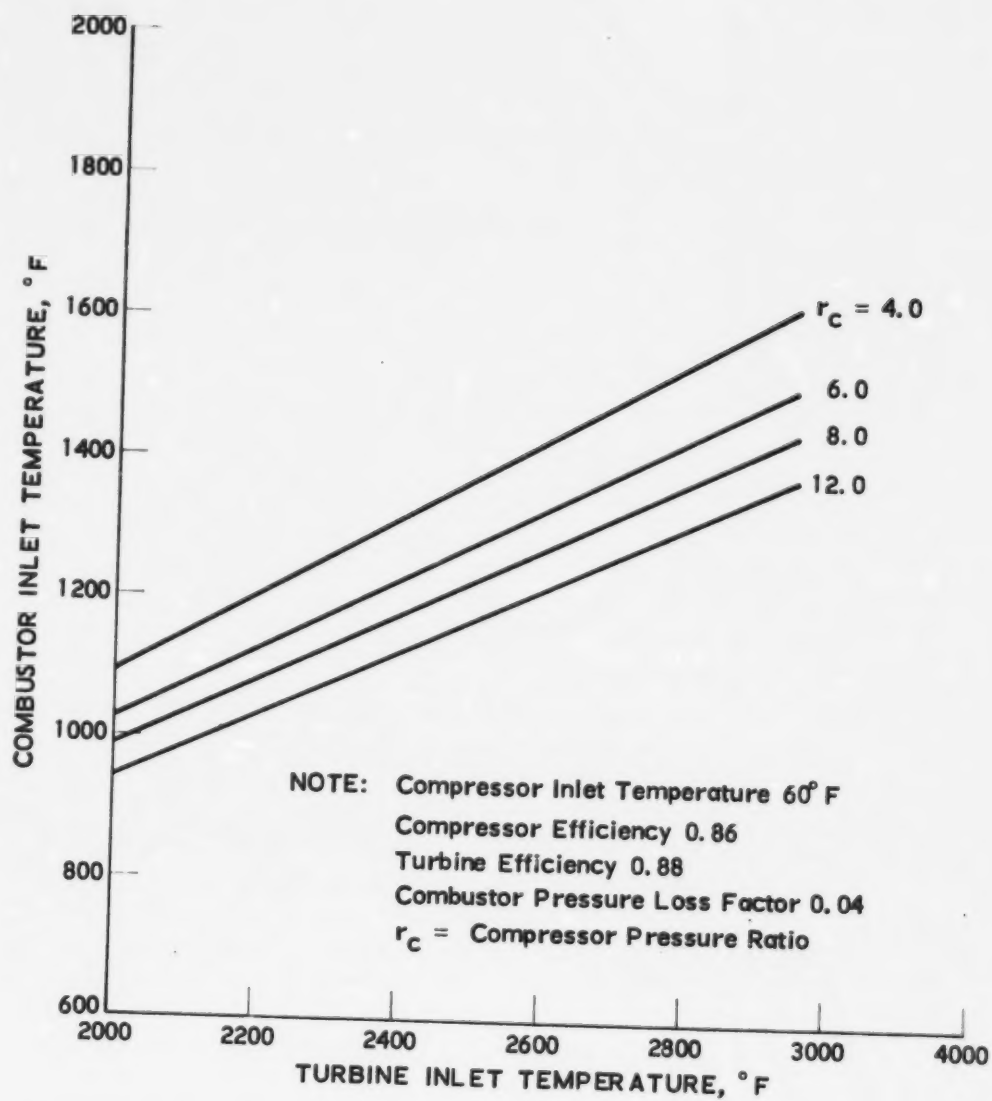


Figure 6-5. Regenerative-Cycle Gas Turbine Combustor Inlet Temperature vs Turbine Inlet Temperature-Regenerator Effectiveness 0.70

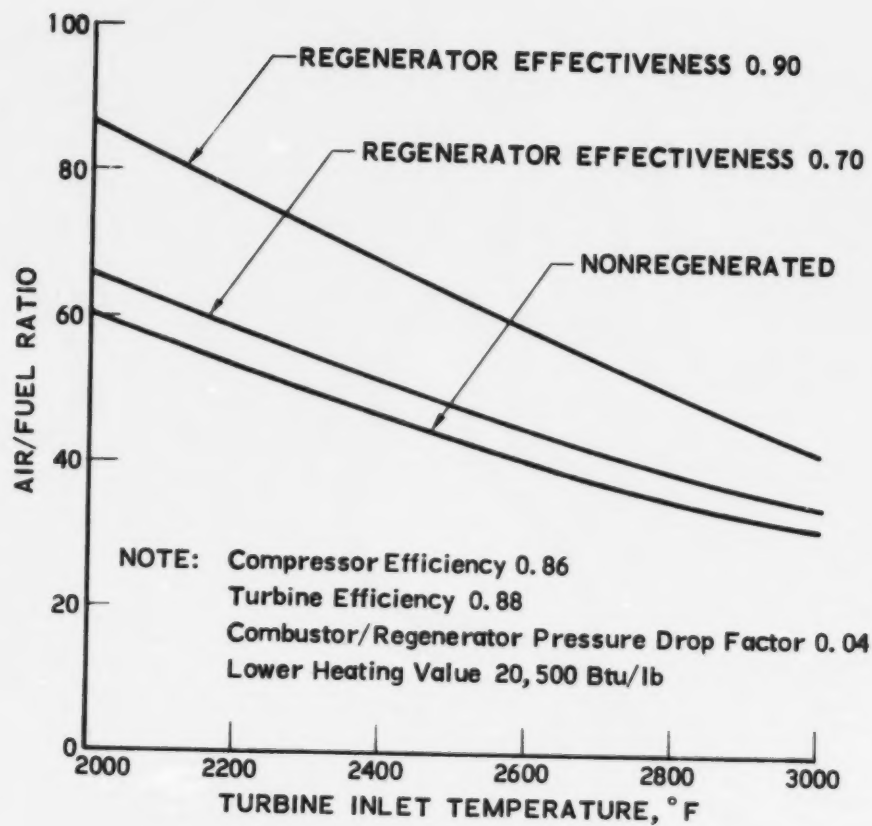


Figure 6-6. Predicted Air-Fuel Ratio vs Turbine Inlet Temperature (Natural Gas)

Table 6-1. NO_x and CO Emissions for Gas Turbines and Steam Power Plants

Case	Unit	Emissions					Comments
		NO _x		CO			
		ppm	lb/MW-hr	ppm	lb/MW-hr	lb/MW-hr	
1	Curtiss-Wright gas turbine	-	6.7	-	-	-	Without water injection
2	Curtiss-Wright gas turbine	-	3.0	-	-	-	With water injection
3	Small industrial gas turbines	-	8.8	-	-	2.9	
4	Typical aircraft gas turbines ⁽¹⁾	-	12.3	-	-	0.4	JT8D engines; full power
5	Ford EVC combustor concept ⁽²⁾	-	0.17	-	-	1.0	Conceptual design
6	Uncontrolled steam plant	400	4.2	<50	<50	0.32	
7	Projected steam plant ⁽³⁾	42	0.44	<100	<100	0.64	Off-stoichiometric burning and flue gas recirculation

(1) (Ref. 6-3)

(2) Externally vaporizing combustor (Refs. 6-4 and 6-5)

(3) Los Angeles Scattergood No. 3 (Ref. 6-6)

⁽¹⁾ (Ref. 6-3)

⁽²⁾ Externally vaporizing combustor (Refs. 6-4 and 6-5)

⁽³⁾ Los Angeles Scattergood No. 3 (Ref. 6-6)

Ford Motor Company for their new externally vaporizing combustor (EVC) concept currently under development for potential use in automotive gas turbines. For comparison, the NO_x and CO emissions of uncontrolled and NO_x -controlled steam power plants are also included in Table 6-1 (cases 6 and 7).

The emissions from a Curtiss-Wright peaking power unit, powered by a Pratt & Whitney GG4C1-D gas turbine, are listed as cases 1 and 2. Without water injection, the NO_x emissions from this unit reach the permissible limit of 140 lb/hr, specified by the Los Angeles County Air Pollution Control District Rule 67, at a derated power setting of about 21 MW. Incorporation of water injection results in a 55 percent reduction of the specific NO_x mass emissions. Carbon monoxide data are not available for this engine.

Case 3 represents a number of small industrial gas turbines generating a net power output of the order of 500 kW (Ref 6-7). The NO_x emissions from these engines are comparable to those of large industrial units exemplified in case 1 by the Curtiss-Wright engine without water injection.

The full-power NO_x and CO emissions of typical state-of-the-art aircraft gas turbines are shown in Table 6-1, case 4. As indicated, NO_x is somewhat higher than for the industrial units, reflecting the higher operating temperatures of the aircraft engines. Conversely, CO is quite low and comparable to steam power plants. The AFAPL projects NO_x emission reductions up to 75 percent, to be accomplished by means of combustor modifications and water injection (Ref. 6-8).

Case 5 shows the NO_x and CO mass emissions computed from Ford's published EVC concept test data (Refs. 6-4 and 6-5). In this combustor design, shown schematically in Figure 6-7, the fuel enters the prevaporization-mixing chamber through a coaxial nozzle and is then atomized and vaporized by the high velocity primary air flow. Ideally, complete vaporization of the fuel droplets is accomplished in the chamber before the fuel-air mixture enters the primary

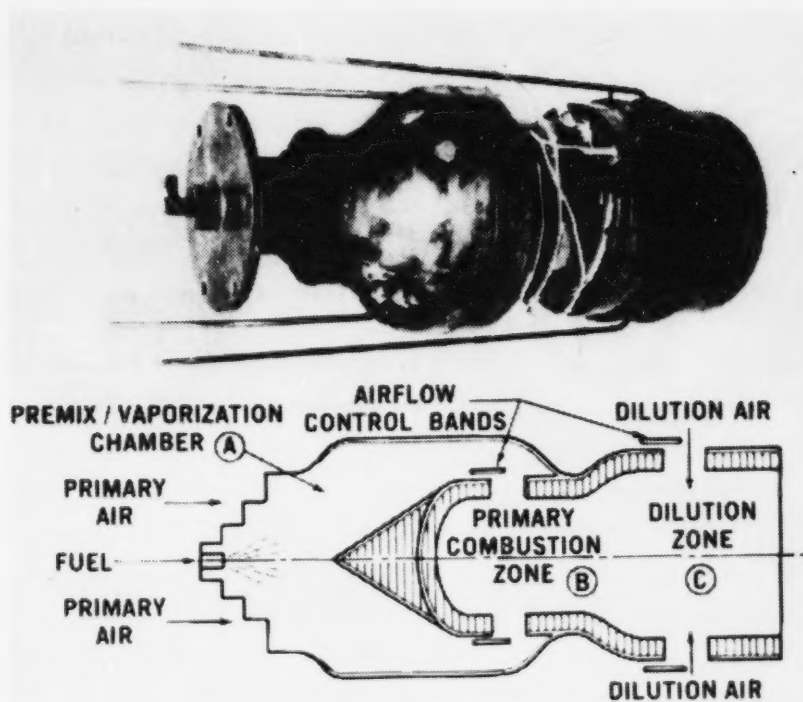


Figure 6-7. Ford Experimental Externally Vaporizing Combustor (EVC) (Ref. 6-5)

combustion zone through a set of adjustable inlet ports. The primary zone fuel-air equivalence ratio is controlled between 0.35 and 0.5 at all times to limit the combustion temperature to about 2800°F to 3000°F. At these temperature levels, only minute amounts of NO_x are formed. Secondary air is then added in the dilution zone of the combustor to obtain the desired turbine inlet temperature. The corresponding CO mass emissions reported by Ford for this combustor are approximately three times higher than for NO_x. However, it is the opinion of Ford that CO could be reduced substantially by increasing the length (volume) of the combustion chamber to permit completion of the CO oxidation reactions. Based on Ford's initial tests, it is concluded that the EVC concept has the potential of achieving very low NO_x emissions. However, a number of potential problem areas must be evaluated before this combustor is ready for use in gas turbines. Potential problem areas include combustor instability, preignition, startup, and durability.

Catalytic combustors and porous-plate surface combustors also offer low emissions potential. In these configurations, the air-fuel ratio of the mixture entering the combustor is adjusted to limit the combustion temperature to sufficiently low levels where the NO formation rate is low. Exploratory tests conducted by Engelhard and the EPA indicate that very low emissions can indeed be achieved with catalytic combustors. In the Engelhard program, the catalyst was operated at air-fuel ratios of about 40:1, system pressures up to 5 atm and air preheat temperatures up to 500°C. Under these conditions, the NO_x was undetectable, HC was less than 10 ppm, and CO was less than 60 ppm. The data from the EPA program are in reasonable agreement with Engelhard's results.

Porous-plate combustor tests conducted by General Electric at 1 atm indicate NO_x emissions substantially below the 1976 Federal emission standards for light-duty vehicles. However, the corresponding CO standard was exceeded in some of the tests.

NO_x EMISSION GOALS FOR LARGE POWER INSTALLATIONS

The applicability of gas turbines to large base power generating systems is governed by two major factors, i. e., cycle efficiency and exhaust emissions.

With regard to cycle efficiency, the specific fuel consumption of the gas turbine must be competitive with existing steam power plants. As discussed in Section 6-1, this requires substantial advances in the state-of-the-art technology, including incorporation of high effectiveness regenerators or recuperators and operation at much higher turbine inlet temperatures.

The emission data listed in Table 6-1 indicate that the NO_x mass emissions of current state-of-the-art gas turbines are an order of magnitude higher than the emissions projected by the Los Angeles Department of Water and Power for its new Scattergood No. 3 steam plant. This particular plant is designed to incorporate flue gas recirculation and off-stoichiometric combustion, and is scheduled to go into service in 1974 at a derated power output level of 315 megawatts (460 MW rated power).

The permissible NO_x concentrations in the exhaust of a hypothetical 315 MW gas turbine power plant meeting the Los Angeles County Air Pollution Rule 67 (140 lb NO₂/hr) are presented in Figure 6-8 for simple-cycle and regenerative-cycle gas turbines, respectively. These values were computed on the basis of the gas turbine operating parameters depicted in Figures 6-1 through 6-6. As illustrated, the allowable NO_x concentrations are extremely low by current standards, especially for highly regenerated gas turbines. The allowable NO_x concentration increases somewhat with increasing turbine inlet temperature as a result of lower engine flow rates per unit power output.

These examples illustrate that the NO_x emissions from current gas turbines require an order of magnitude reduction before the engines become feasible for use in large base power generating units. Since conventional droplet burning combustor concepts are severely limited with respect to NO_x emission

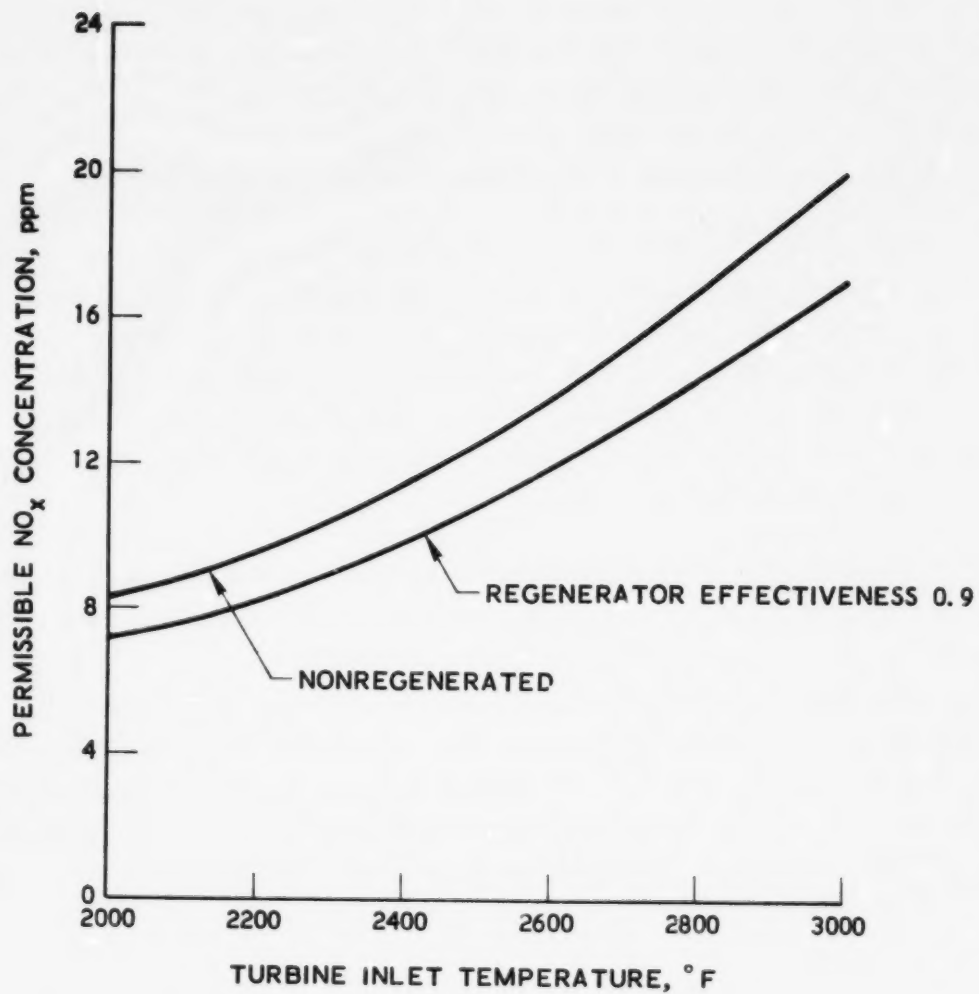


Figure 6-8. Permissible Gas Turbine NO_x Concentrations to meet Rule 67 of the Los Angeles Air Pollution Control District (315 MW Power Output)

reduction, it is concluded that new combustor designs of the prevaporization/premixing type are needed to meet the low NO_x emission requirements with gas turbines. Catalytic and possibly porous-plate surface combustors have the potential to meet these requirements.

6.5

FUEL PREPARATION AND PREIGNITION PROBLEMS

Catalytic combustors require a completely prevaporized and uniformly distributed air-fuel mixture at the catalyst inlet to prevent the excessive temperatures that might result from droplet burning on the catalyst surface. Therefore, catalytic combustors are limited to gaseous fuels such as methane, propane, natural gas, and coal gas and certain distillate fuels including gasoline and kerosene.

Recognizing these requirements, NASA/Lewis and the AFAPL are currently working on the development of a number of different fuel atomization and prevaporization-mixing approaches. These systems are designed to provide a uniform fuel vapor-air mixture at the inlet to the catalytic combustor section under all operating conditions of the gas turbine. For stationary gas turbines, which are generally operated at semisteady-state conditions, the design requirements for the prevaporization-mixing chamber might be less stringent.

In prevaporized-premixed systems, mixture preignition represents a potential problem area which requires special design consideration for several reasons. For instance, preignition of the mixture before completion of the fuel vaporization-mixing process could result in severe local overtemperature conditions leading to catalyst and substrate failure. On the other hand, preignition of a completely vaporized and premixed air-fuel charge could seriously compromise the effectiveness of the catalyst in those designs in which a high porosity γ -alumina wash coat is applied to enhance catalyst lightoff. If these catalyst sections are exposed to temperatures in excess of about 1750°F , the γ -alumina is converted to the low porosity α -phase, resulting in a very substantial reduction in the number of active catalyst sites.

The autoignition temperatures of methane and kerosene are depicted in Figure 6-9 as a function of operating pressure (Ref. 6-9). As illustrated, the autoignition temperatures of these fuels decrease with increasing pressure level. Based on an extrapolation of the available methane data, it appears that the autoignition temperature of methane is higher than the combustor air inlet temperature predicted for simple-cycle gas turbines operating at compressor pressure ratios up to about 25:1 (Figure 6-3). Therefore, it is unlikely that preignition of methane-air mixtures would occur in these particular engines. Conversely, in regenerated gas turbines, the combustor air inlet temperatures shown in Figures 6-4 and 6-5 are sufficiently high for most designs to permit preignition of methane-air mixtures. Because of the lower autoignition temperature of kerosene, preignition could occur with this fuel at the operating conditions of most simple-cycle and regenerative-cycle gas turbines.

The occurrence of preignition is affected also by a number of additional parameters, including fuel-air mixture ratio and ignition delay time. As shown in Figure 6-10, each fuel has a minimum concentration below which autoignition cannot take place (Ref. 6-10). This concentration, called the "lower flammability limit," decreases with increasing mixture temperature. For the various simple-cycle and regenerative-cycle gas turbines, the fuel-air mixture entering the combustor is sufficiently rich to permit ignition of all turbine inlet temperatures above about 2100°F.

The ignition delays for kerosene and gasoline in air at atmospheric pressure are presented in Figure 6-11 as a function of air temperature (Ref. 6-4). At elevated pressures, the delay times tend to be somewhat higher. In general, the ignition delay time of the various fuels, which is composed of physical delay time and chemical delay time, decreases with increasing air temperature. The physical delay accounts for the elapsed time between fuel injection and the formation of a combustible mixture and subsequent heating of the mixture to the autoignition temperature. The chemical delay is the time from the beginning of perceptible chemical reaction to the occurrence of autoignition. The physical and chemical delay times of gasoline and kerosene are of comparable

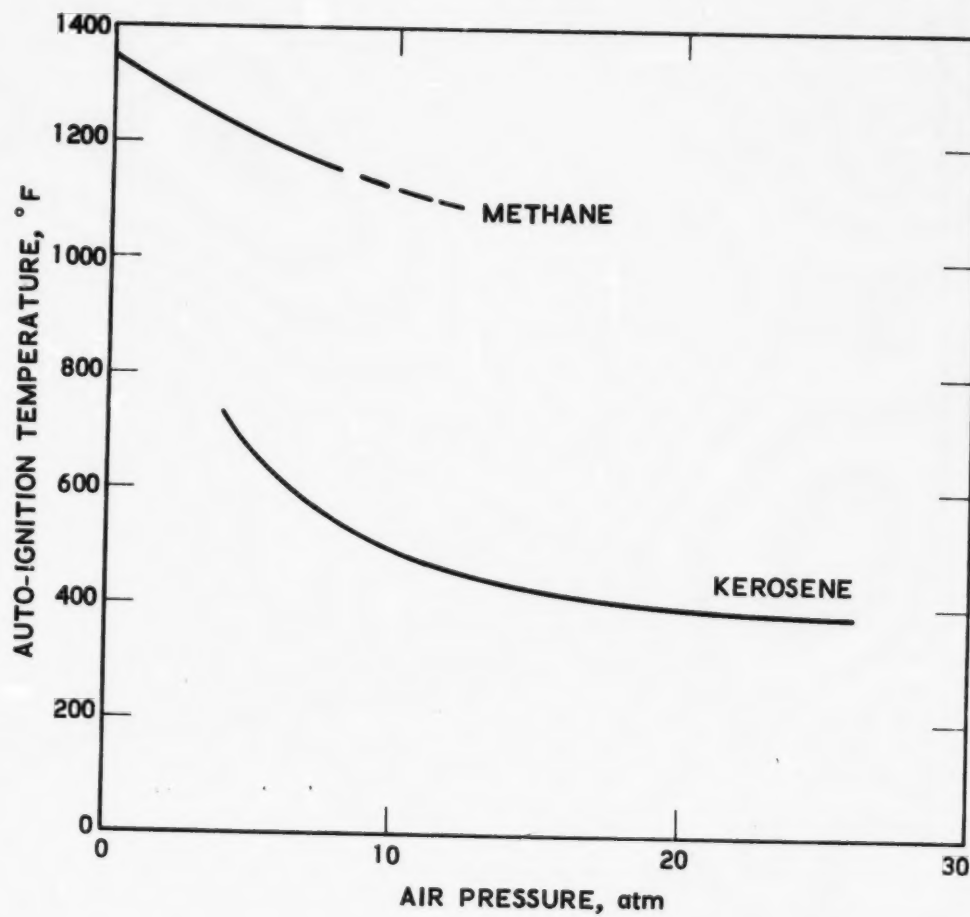


Figure 6-9. Autoignition Temperatures for Methane and Kerosene vs Pressure (Ref 6-9)

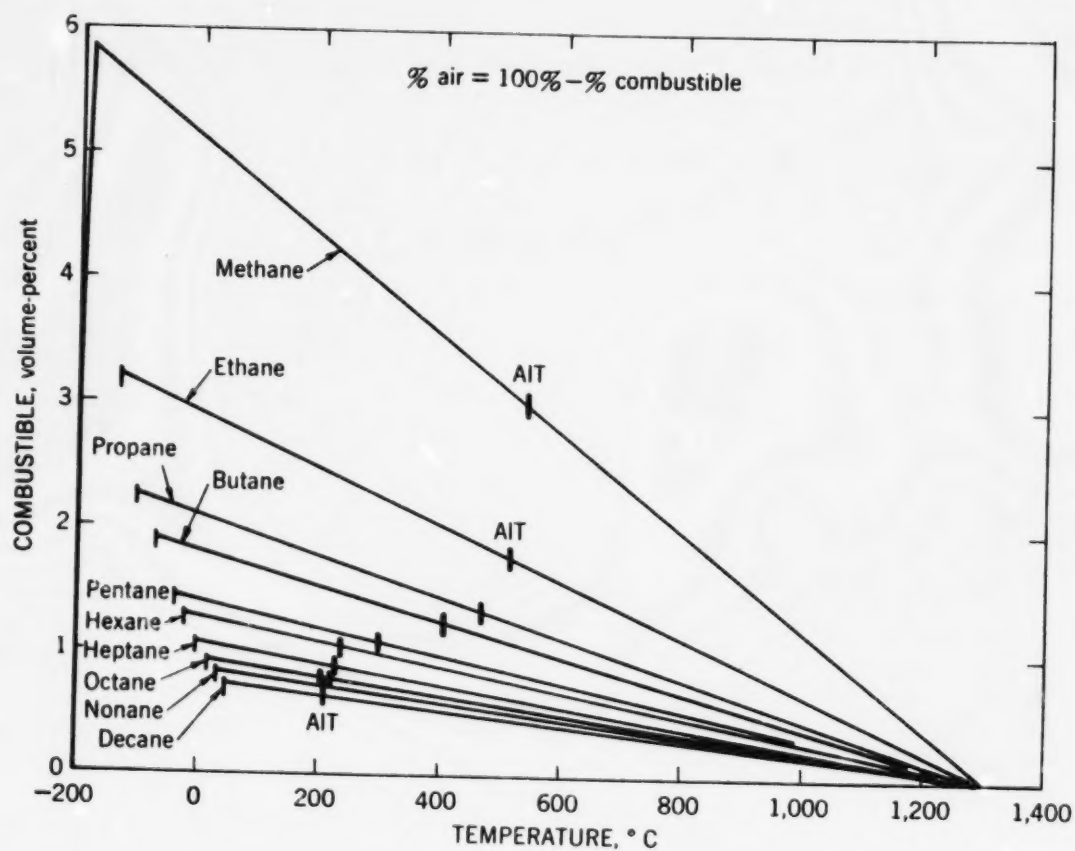


Figure 6-10. Effect of Temperature on Lower Limits of Flammability of 10 Paraffin Hydrocarbons in Air at Atmospheric Pressure (Ref. 6-10)

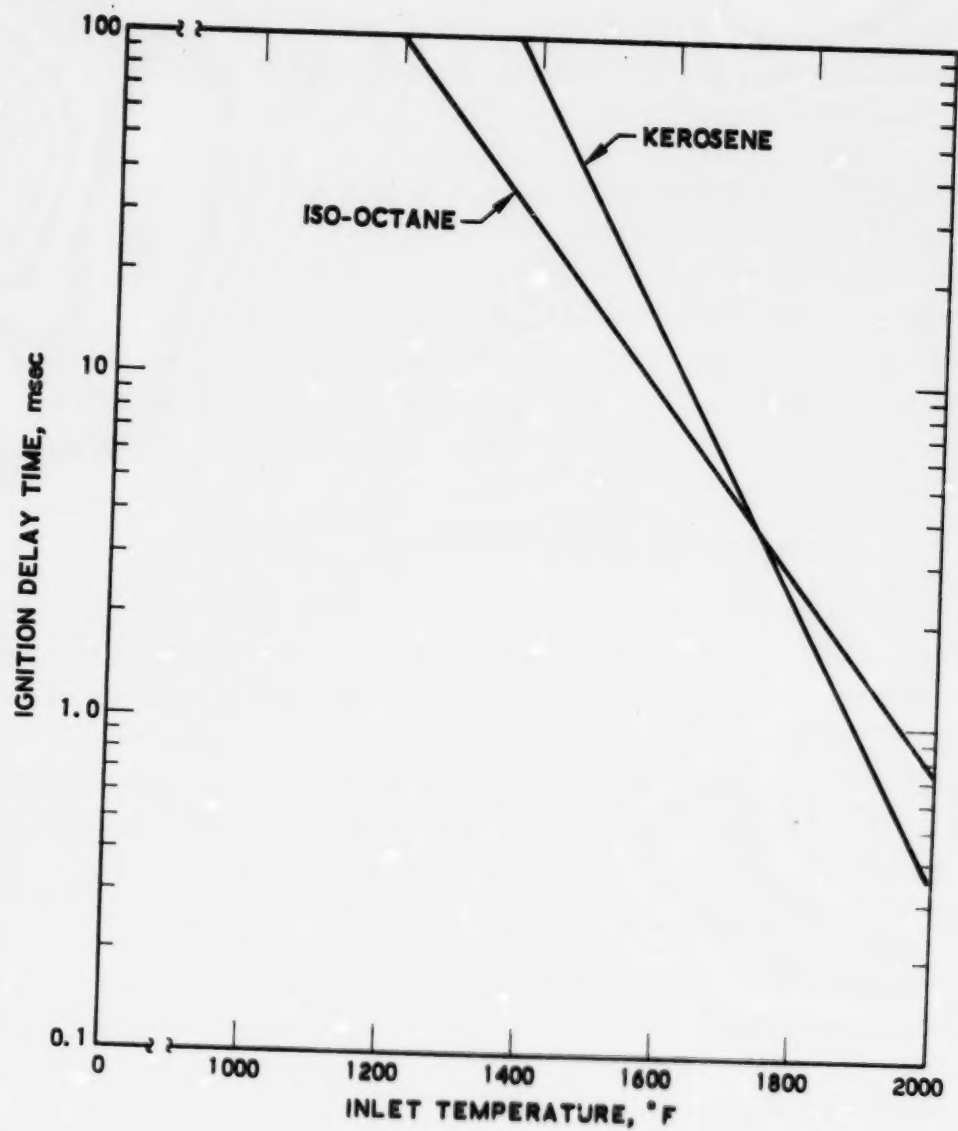


Figure 6-11. Ignition Delay Time vs Inlet Temperature at 1 Atmosphere (Ref. 6-4)

magnitude, but overlap each other to some degree (Ref. 6-11). No reliable data have been found for methane. However, there are indications that the ignition delay times of gaseous methane are somewhat higher than the combined physical and chemical delays shown in Figure 6-11 for kerosene (Ref. 6-11).

Based on these considerations, it is concluded that the ignition delay times for kerosene and gasoline are sufficiently short to create a potential pre-ignition problem in gas turbine combustors utilizing prevaporized fuel-air mixtures. With methane, preignition is probably limited to regenerated gas turbines, in which the combustor inlet temperature is generally above the autoignition temperature. In these cases, special care must be exercised in the design of the prevaporization-mixing chamber. These aspects are further discussed in the following section.

6.6 CATALYTIC COMBUSTORS

6.6.1 Catalytic Combustor Design Parameters

A number of important parameters affecting the design and optimization of catalytic gas turbine combustors have been identified during this study. These include various approaches to minimize emissions, housing design, catalyst and substrate configurations, combustor sizing, lightoff procedures, and fuel preparation. These are briefly discussed in the following paragraphs.

6.6.1.1 Emissions

The low emission potential of catalytic combustors operating at temperatures of about 2000°F has been demonstrated. Consistent with theoretical predictions, the observed NO_x emissions are practically zero and the CO and HC emissions are very low and comparable to current gas turbines. Further reductions of the CO and HC might be possible by increasing the operating temperature of the unit, consistent with the temperature limitations of the catalyst and substrate materials. This could be accomplished by using

only a portion of the total compressor air in the combustor and adding the remainder in a secondary combustion zone located between the catalytic unit and the turbine nozzle inlet. Another possible approach to reduce the HC and CO emissions involves increasing the residence time of the combustion gases in the high-temperature zone by means of a reduction of the design specific heat release rate of the catalytic combustor. Although the associated increase in combustor volume might preclude the application of this approach to automotive and aircraft gas turbines, it might well be feasible for stationary gas turbines, which generally have less restrictive volume limitations.

6.6.1.2 Housing Design

To minimize the outer temperature of the catalyst housing and quenching of the chemical reactions in the wall zone, insulation of the inside surfaces of the housing is mandatory. The mechanical and thermal integrity of the insulation requires experimental verification under simulated gas turbine operating conditions.

6.6.1.3 Catalyst and Substrate Configuration

Currently, very little information is available regarding the catalyst and substrate materials composition and the important design parameters, which are considered proprietary by the manufacturers. Basically, either pellet or monolithic substrate configurations are considered applicable to catalytic combustors. Both types are currently utilized in industrial and automotive catalyst systems. In automotive applications, catalyst failures due to engine vibrations have occurred in the past, especially on four-cylinder engines. Under normal operating conditions, the vibration levels in gas turbines are very low; as a result, catalyst failure due to vibrational loads is not considered to be a major problem area for catalytic gas turbine combustors. The monoliths currently available from American Lava, Corning, and DuPont have a temperature capability of about 2400°F, which is higher than the maximum turbine inlet temperature projected for stationary gas turbines in the 1970 decade. However, substrates manufactured from other materials such as

zirconia, silicon carbide, and alumina would have to be developed for use in the advanced high-temperature gas turbines projected for the late 1980s.

6.6.1.4 Combustor Sizing

Catalytic combustors designed and manufactured by Engelhard are currently being tested by NASA/Lewis and by the AFAPL. Both organizations are optimistic regarding the feasibility of low-emission catalytic combustors for automotive and aircraft gas turbine applications. Since space velocity and specific heat release rate have a direct impact on the required volume of the unit, it is most important to maximize space velocity within the constraints of the desired emission durability performance. This might be accomplished by means of segmentation of the catalyst substrates selected for the various applications. For example, the upstream section of the catalytic combustor might be designed for rapid lightoff through the use of a low lightoff temperature catalyst formulation deposited on a high porosity γ -alumina wash coat. Since γ -alumina is limited to operating temperatures of about 1750°F, other catalyst segments, coated with lower specific surface area materials such as α -alumina, would be required in the high-temperature regions of the combustor. In order to optimize the performance and durability of the unit, various segments might be coated with different catalyst materials, depending upon the fuel and other operating parameters of the particular application.

6.6.1.5 Catalyst Lightoff Procedures

With regard to catalyst lightoff, a number of organizations are currently involved in the development of preheat systems for potential use in catalytic combustors. NASA/Lewis favors electric preheating of the catalyst bed, while AFAPL is concentrating its efforts on a system using waste heat from auxiliary power systems. Engelhard is in the process of evaluating several proprietary concepts designed for use with different fuels. Automotive and aircraft gas turbines require very rapid catalyst lightoff in order to minimize the start delay time of the engine and the cold start emissions. These factors are considered to be less important for stationary gas turbines.

Therefore, preheating of the catalyst could occur more gradually and this would result in lower thermal stresses and longer catalyst life. Electric heaters as well as waste heat and pilot flame preheat techniques are potential candidates for stationary gas turbines.

6.6.1.6 Fuel Preparation

Catalytic combustors are limited to gaseous and distillate liquid fuels. To prevent catalyst failure due to fuel coking or overtemperature conditions, a well designed fuel prevaporization and mixing system is required. This system, located upstream of the catalytic combustor proper, must be large enough to provide complete fuel vaporization and uniform fuel and air mixing, and small enough to prevent preignition of the fuel-air charge in the prevaporization/mixing chamber. The design of the chamber walls requires careful consideration of aerodynamic principles in order to avoid zones of flow separation which might serve as flame holders.

Cost data for catalytic combustors are currently not available. NASA/Lewis intends to conduct a comprehensive economic analysis of catalytic combustors for gas turbines upon completion of its scheduled catalytic combustor feasibility program.

6.6.2 Potential Problem Areas

The low-emission potential of catalytic combustors has been demonstrated by Engelhard and by the EPA in exploratory test programs conducted over limited ranges of simulated gas turbine operating conditions. These initial results are encouraging. However, a number of potential problem areas must be resolved by carefully planned experimental and theoretical investigations before a complete assessment can be conducted regarding the applicability of catalytic combustors to both new and existing stationary gas turbines. These areas, which are briefly highlighted in the following sections, include:

1. Catalyst durability
2. Specific heat release rate
3. Emission characteristics

4. Mechanical integrity
5. Catalyst materials optimization
6. Ignition characteristics

6.6.2.1 Catalyst Durability

The service life of catalysts is most strongly impacted by two factors: catalyst poisoning and substrate degradation. Poisoning of the catalyst by lead, sulfur, and other contaminants contained in the fuel and lubricating oil, and loss in catalyst activity due to overtemperature conditions, are major problem areas in automotive catalysts. In industrial catalysts, temporary deactivation due to fuel coking has been observed in some cases. Poisoning by carbon buildup and by lead and other metal compounds is considered less likely with gaseous and kerosene-type fuels; however, because of the long maintenance-free service life normally demanded from industrial gas turbines, the effects of trace amounts of these contaminants on catalyst durability performance must be systematically evaluated. Conversely, sulfur is found in some natural gas grades and in most distillate fuels considered for use in gas turbines. Prolonged exposure of the catalyst to sulfur compounds could seriously compromise catalyst performance, in spite of the relatively high operating temperatures projected for catalytic gas turbine combustors. Sulfur poisoning, which has created problems in automotive base metal catalysts, has been of less concern in platinum group metal catalysts used in many petrochemical processes. In particular, platinum has shown considerable resistance to poisoning by sulfur.

In stationary gas turbines, which are normally designed to operate at semi-steady-state conditions, overtemperature is not considered a major problem area provided a well functioning fuel prevaporization and mixing system is utilized. However, the effect of temperature excursions on the durability of the projected catalytic combustors requires experimental evaluation to determine the degree of temperature and fuel-air mixture control required for the various projected applications. A loss in catalyst activity would result

primarily in higher CO and HC emissions, and would probably have a very small effect on the NO_x emissions. Therefore, CO and HC represent key parameters which have to be very closely monitored during the course of the recommended catalytic combustor durability program.

Some initial durability testing will be conducted by AFAPL as part of its catalytic combustor feasibility test program. However, the scheduled test duration of about 100 hours is by no means adequate to provide the information required for an assessment of the durability performance of catalytic combustors for stationary gas turbines.

6.6.2.2 Specific Heat Release Rate

The specific heat release rate of the catalytic combustor is an important design parameter affecting the size, weight, and cost of the unit. In general, the CO and the HC emissions from catalytic combustors are expected to decrease as specific heat release rate (or space velocity) is reduced while the NO_x emissions remain essentially constant. To permit optimization of catalytic combustors in terms of size and emission levels, the effects of specific heat release rate on the emissions and pressure drop must be characterized over the ranges of operating conditions projected for the current and future simple-cycle and regenerative-cycle gas turbines.

6.6.2.3 Emission Characteristics

To permit a meaningful assessment of the applicability of catalytic combustors, the lightoff and emission durability characteristics of these devices must be determined for the different fuels as a function of air-fuel mixture ratio, air inlet temperature and pressure, flow rate, and operating time.

In the case of liquid fuels, the effects of fuel-bound nitrogen on the NO_x emissions of catalytic combustors must be evaluated experimentally. It is well known that in conventional combustors, as much as 70 percent of the bound nitrogen is converted to NO_x (Ref. 6-12).

6.6.2.4 Mechanical Integrity

Vibration and thermal stress levels are expected to be relatively low in stationary gas turbine combustors, except perhaps during engine startup. However, experimental evaluation of these parameters is considered mandatory in order to determine the limitations and margins of safety with respect to substrate cracking and chipping of the various projected catalyst, substrate, and container configurations.

6.6.2.5 Catalyst Materials and Loading Requirements

Although Engelhard has presumably selected the best currently known catalyst and substrate combination, it is recommended that an independent catalyst screening program be conducted. The optimum catalyst formulation and combustor design for the various fuels, fuel contaminants, and projected ranges of turbine operating parameters should be determined. If platinum group metals are used in the catalyst formulation, the effects of metal loading on catalyst lightoff and emission durability performance should be evaluated as part of the proposed screening program. These are very important aspects which impact the tradeoffs between catalyst cost, size, and performance characteristics, and possibly even the world platinum group metal supply and demand balance.

6.6.2.6 Ignition Characteristics

The optimum catalyst preheat temperature, flow rate, air-fuel ratio, and air pressure required for smooth lightoff are currently not known and should be determined for the fuels of interest. Also, the operational characteristics of the fuel atomization, prevaporization, and mixing systems must be thoroughly evaluated for the various fuels and system applications. These devices are required to provide a uniform fuel vapor-air mixture at the combustor inlet over the full range of engine operating conditions, without the occurrence of preignition.

6.7

POROUS-PLATE SURFACE COMBUSTORS

6.7.1

Introduction

Like catalytic combustors, the sintered metal porous-plate combustor concept offers the potential of very low NO_x emissions when the combustor is operated below the adiabatic flame temperature.

Evaluation of this concept for steam boilers has indicated that porous-plate surface combustors might be feasible for use in low-pressure applications. However, at the elevated system pressures typical of gas turbines, the heat transferred back to the burner plate increases proportionately and removal of this heat at acceptable surface temperatures creates a serious problem area. Although a detailed analysis of these parameters is beyond the scope of this study, it is considered appropriate to briefly discuss the important design parameters impacting the design of porous-plate surface combustors for simple-cycle, regenerative-cycle, and combined-cycle stationary gas turbines.

6.7.2

Discussion

General Electric, under contract to the EPA, is currently involved in the development of a porous-plate combustor for potential use in automotive gas turbines (Ref. 6-13). In the course of this program, General Electric has examined the effects of pressure and air inlet temperature on the operational characteristics of various radiation-cooled and internally cooled burner configurations. With radiation-cooled burners, flashback has occurred on several occasions, especially at higher system pressures. At a fuel-air equivalence ratio of 0.9 and a system pressure of 3 atm, the measured back face temperature of the porous burner plate was 1400°F , reflecting the higher heat flux into the plate. Under these conditions, preignition of the fuel-air mixture has occurred at the inlet to the burner. Attempts to prevent flashback by means of various types of insulating schemes were unsuccessful. However, by reducing the equivalence ratio to 0.7, the burner has been operated successfully at pressures up to 4 atm without the occurrence of flashback.

Because of the limited capability of radiation-cooled burners, General Electric is now concentrating its efforts on internally cooled porous sintered metal combustors of the type illustrated in Figure 6-12. In this design, part of the heat transferred back to the plate is removed by the coolant, and the remainder by radiation. The higher cooling capacity of the unit results in a lower burner surface temperature. Preliminary indications are that this concept might be developed into a viable design for use in automotive gas turbines, operating at design point system pressures of about 4 atm. However, because of the high coolant air temperatures of highly regenerated gas turbines, the development of new porous metals with a higher temperature capability might be required for these applications.

Current simple-cycle stationary gas turbines operate at pressures of the order of 15 to 20 atm, and even higher pressures are projected for advanced designs. At these elevated pressure levels, the heat load of the porous-plate combustor is much higher than in steam boilers and automotive gas turbines, resulting in high surface temperatures and large temperature differences across the burner plate and imbedded tube materials. The severe temperature and thermal stress conditions might be alleviated to some degree by operating the burner at very low equivalence ratios. However, under these conditions, the burner surface area and volume requirements increase substantially, creating a potential packaging problem. Furthermore, less cooling air is available in this case, which tends to further increase the size of the burner.

In highly regenerated stationary gas turbines, the optimum system pressure is about 4 to 6 atm, which is comparable to automotive gas turbines. As a result, the heat flux to the burner is reduced and the concept might be feasible for these particular applications. However, in regenerative gas turbines, the temperature of the coolant air is very high, especially in the case of the elevated turbine inlet temperature levels projected for advanced gas turbines. This would result in even higher burner surface temperatures.

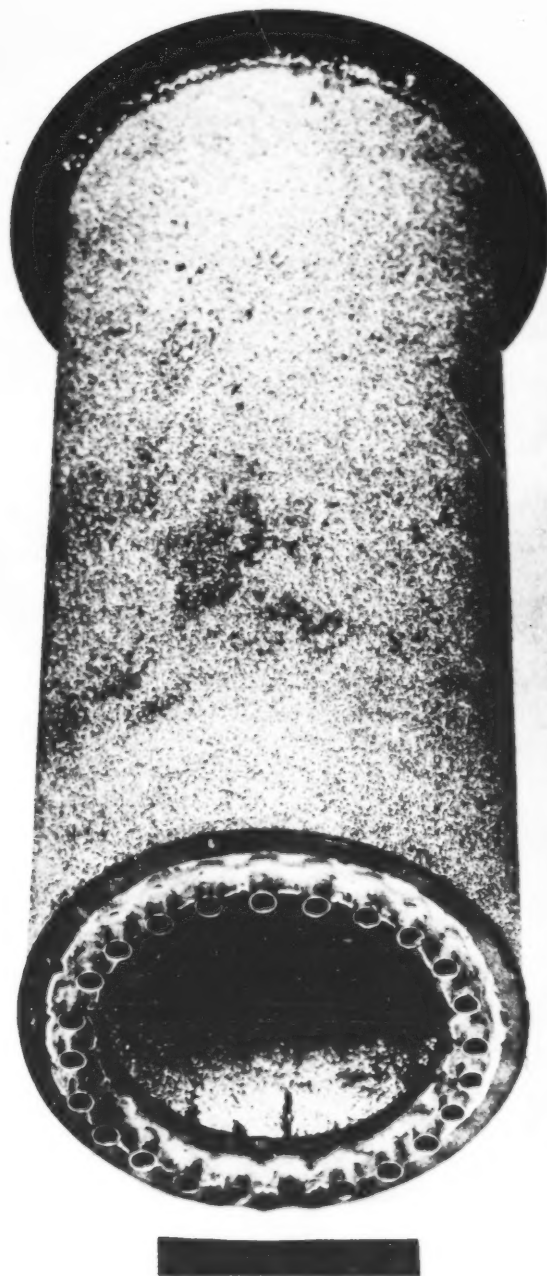


Figure 6-12. General Electric Air-cooled Burner No. 106
During Fabrication

In combined gas turbine-steam turbine cycles, the porous-plate cooling problems could be alleviated to some degree by using water from the steam turbine cycle to cool the porous plate combustor.

6.7.3 Conclusions

Cooling of porous-plate surface combustors by radiation alone is not considered practical at the elevated system pressures of simple-cycle and regenerative-cycle gas turbines. However, porous metal designs utilizing imbedded cooling tubes represent a possible design approach for low-pressure gas turbines of the type used in automotive or highly regenerated stationary gas turbines and for combined gas turbine-steam turbine cycles. Considerably more research and development work is required, especially in the sintered metals area, before the concept can be seriously considered for application in simple-cycle, regenerative-cycle, and combined-cycle stationary gas turbines.

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- 6-13. R. J. Rossbach, Development of Low-emission Porous-plate Combustors for Automotive Gas Turbine and Rankine Cycle Engines, Quarterly Progress Report GESP-738, General Electric Company, Cincinnati, O. (May 1973).

APPENDIX A

VISITS AND CONTACTS

A-1

ORGANIZATIONS VISITED

<u>Organization</u>	<u>Date of Visit</u>	<u>Primary Contact(s)</u>
Institute of Gas Technology Chicago, Illinois	November 1, 1972	Mr. D. Larson Dr. R. Rosenberg
Perfection Products Company Waynesboro, Georgia	November 2, 1972	Dr. P. Goodell
Burnham Corporation Lancaster, Pennsylvania	April 2, 1973	Mr. R. Givler Mr. R. Reichhelm
Selas Corporation of America Dresher, Pennsylvania	April 2, 1973	Dr. C. Gottschlich
Engelhard Minerals & Chemicals Corp. Engelhard Industries Division Murray Hill, New Jersey	April 3, 1973	Dr. G. Gillespie Dr. R. Carrubba Mr. R. Heck
Air Force Aero Propulsion Laboratory Dayton, Ohio	April 4, 1973	Capt. W. Blazowski
American Gas Association Cleveland, Ohio	April 5, 1973	Dr. D. DeWerth
NASA/Lewis Research Center Cleveland, Ohio	April 6, 1973	Mr. J. Heller Mr. T. Mroz
General Electric Company Energy Systems Programs Cincinnati, Ohio	April 6, 1973	Mr. R. Rossbach

ORGANIZATIONS CONTACTED BY TELEPHONE

<u>Organization</u>	<u>Date of Visit</u>	<u>Primary Contact</u>
A. F. Holden Company Milford, Michigan	December 8, 1972	Mr. K. Kuhn
Oxy Catalyst Inc. West Chester, Pennsylvania	January 19, 1973	Mr. J. Houdry
Matthey Bishop, Inc. Malvern, Pennsylvania	January 19, 1973	Dr. A. Khuri
Impala Industries Wichita, Kansas	January 23, 1973	Mr. J. Smith
Zebco Tulsa, Oklahoma	January 23, 1973	Mr. W. Duncan
Combustion Engineering New York, N. Y.	January 23, 1973	Dr. Ulmer
Coleman Company Wichita, Kansas	January 23, 1973	Mr. F. Smith
Shell Oil Company Wood River, Illinois	February 5, 1973	Mr. L. Graiff
Argonne National Laboratories Argonne, Illinois	February 5, 1973	Dr. A. Jonke
Pope Evans Alexandria, Virginia	February 5, 1973	Mr. S. Ehrlich
Solar San Diego, California	February 5, 1973	Mr. W. A. Compton
Westinghouse Electric Corp. Pittsburgh, Pennsylvania	February 5, 1973	Mr. D. Archer
Esso Research & Engineering Co. Linden, New Jersey	February 6, 1973	Mr. A. Skopp
Gulf Oil Corporation Harmerville, Pennsylvania	February 8, 1973	Dr. B. Taylor
Office of Coal Research Washington, D. C.	February 23, 1973	Dr. G. Hill

<u>Organization</u>	<u>Date of Visit</u>	<u>Primary Contact</u>
Ford Motor Company Dearborn, Michigan	May 29, 1973	Mr. W. Wade
City Administration Burbank, California	May 29, 1973	Mr. J. Hall
Dept. of Water and Power City of Los Angeles Los Angeles, California	June 7, 1973	Mr. N. Bassin

APPENDIX B

UNITS OF MEASURE--CONVERSIONS

Environmental Protection Agency policy is to express all measurements in Agency documents in metric units. With a few exceptions, this report uses British units of measure. For conversion to the metric system, use the following conversions:

To convert from	to	Multiply by
$^{\circ}\text{F}$	$^{\circ}\text{C}$	$5/9 (^{\circ}\text{F}-32)$
ft	meters	0.304
ft^2	meters^2	0.0929
ft^3	meters^3	0.0283
in	cm	2.54
in^2	cm^2	6.45
BTU	kcal	0.252
BTU/ft^3	kcal/m^3	8.90
$\text{BTU}/\text{hr}\text{-ft}^2$	$\text{kcal}/\text{hr}\text{-m}^2$	2.71
BTU/lb	cal/gm	0.556
BTU/in^2	kcal/cm^2	0.039
$\text{ft}^3/\text{min}\text{-in}^2$	$\text{m}^3/\text{min}\text{-cm}^2$	0.00439
$\text{lb}/10^6 \text{ BTU}$	$\text{gm}/10^6 \text{ cal}$	1.80
lb/in^2	mm Hg	51.71
gal/hr	l/hr	3.78
hp	kW	0.746